AUGUST, 1953

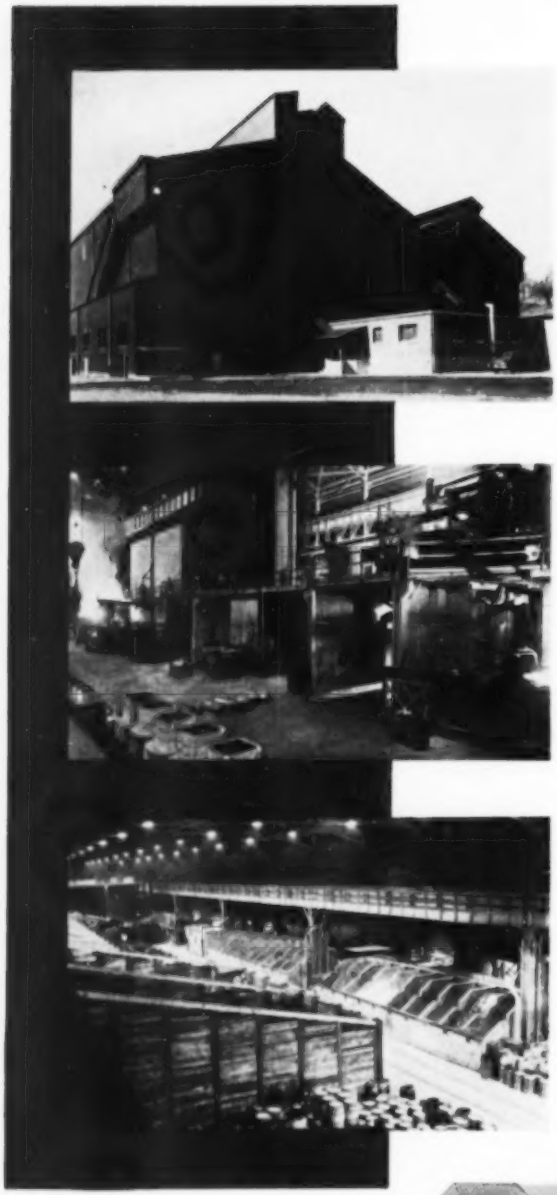
Journal of METALS

August JOURNAL OF METALS Highlights:

"Design Features of Fairless Works Open Hearth" - p. 976
"Ion Exchange Finds Wider Use in Concentration and Recovery of Metals from Dilute Solutions" - p. 980

Freyn-Design

ELECTRIC FURNACE SHOPS



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Constructed For
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Journal of METALS

VOL. 5, NO. 8 AUGUST, 1953

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COVER

These four Zeo-Karb H units of a Permutit demineralizing and silica removal installation in a large Houston oil refinery are similar to units employed in extractive metallurgy. Capacity of the installation is 1600 gpm. For a summary of available information on hydrometallurgical applications of ion exchange, see article p. 980.

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Meet The Authors

F. L. CARR

G. VAUX

F. L. Carr (p. 998), a native of Lowell, Mass., was in the physical metallurgy branch of the Watertown Arsenal Laboratory for five years. Since 1951 he has been associated with the metallurgical dept., National Research Corp., Cambridge, Mass. He is presently engaged in the supervision of the metallurgical laboratory. He has co-authored several papers on temper brittleness. On the lighter side of his hobbies, Mr. Carr directs a dance orchestra.

George Vaux (p. 1038) received his B.Sc. from Haverford College in 1930 and attended the Imperial College of Science, London University (DIC), in 1937. Mr. Vaux has taught physics at both the University of Pennsylvania and Haverford College. He attended the Naval Academy postgraduate school and was on active duty as a Naval Reserve Officer from 1942 to 1947. During this time he was administrator of scientific programs, ONR. For one year Mr. Vaux was physicist, Engineering Research Associates, Washington, D. C. He joined the New Jersey Zinc Co., Palmerton, Pa., as investigator, X-ray diffraction in 1949. He has been treasurer and director of development, Spitz Laboratories, Inc., Philadelphia since 1951.

M. Goldman (p. 998) is a graduate of Boston University and Tufts College. From 1949 to 1952 Mr. Goldman was a physical chemist with the Watertown Arsenal. He then joined the staff of Battelle Memorial Institute as principal chemist and resigned in May 1953 to accept the position of engineer senior metallurgist with Goodyear Aircraft Corp., Akron, Ohio.

T. R. A. DAVEY

M. J. SINNOTT

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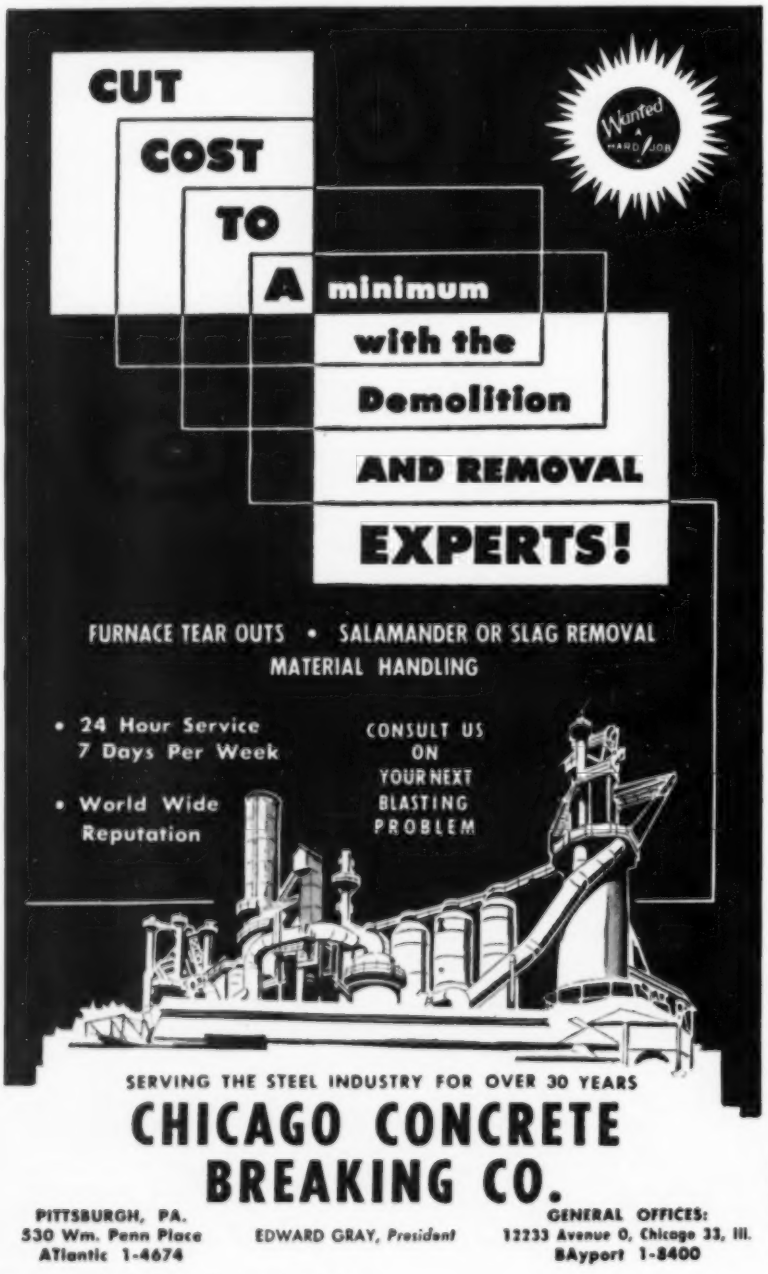
M. J. Sinnott (p. 1016), associate professor of chemical engineering, University of Michigan, is a graduate of that institution (B.S., M.S., and Sc.D.). Dr. Sinnott began his career as plant metallurgist with the Great Lakes Steel Corp. in 1938. For three years he was research associate of the University of Michigan, and in 1940 joined Goodyear Aircraft Corp. He was senior research and development engineer at Goodyear before rejoining the staff at the University. He is a member of various professional societies, including AIME.



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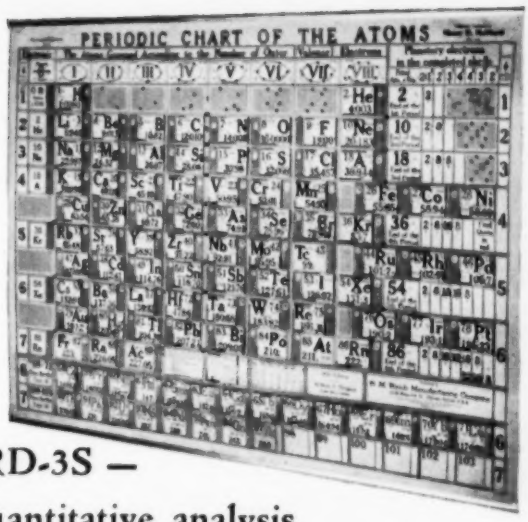

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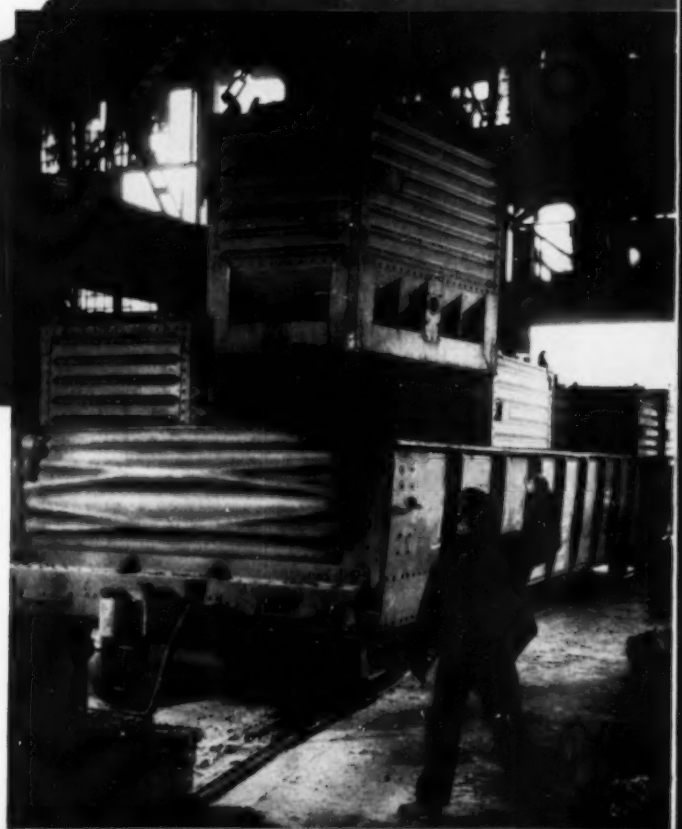

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For additional information phone, wire, or write one of the ELECTROMET *offices. Ask for the* ELECTROMET *booklet entitled, "Melting Low-Carbon Stainless Steel." It shows the advantages that can be obtained in producing low-carbon stainless steel with* SIMPLEX *ferrochrome.*

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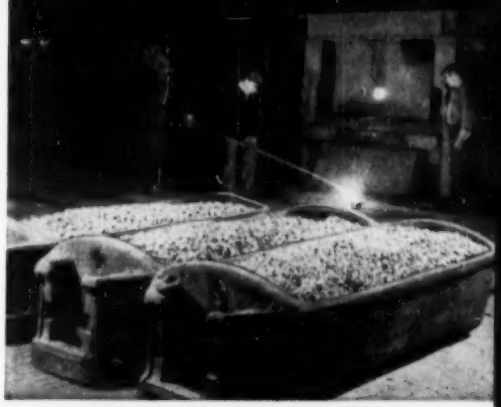
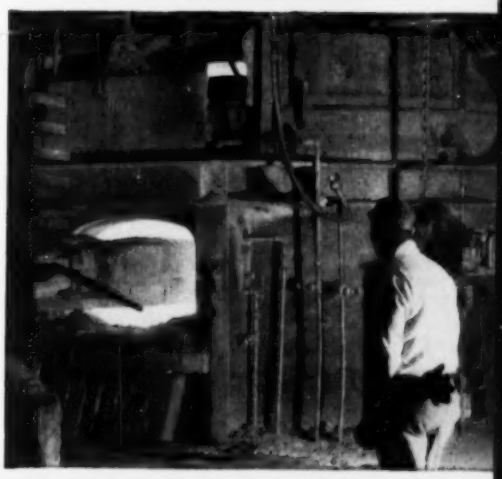
2 LOW CARBON CONTENT

Here is the new SIMPLEX ferrochrome ready for charging in the production of a heat of extra-low-carbon stainless steel. The carbon content of the pellets is so low that the addition of SIMPLEX ferrochrome will not increase the carbon content of the bath.



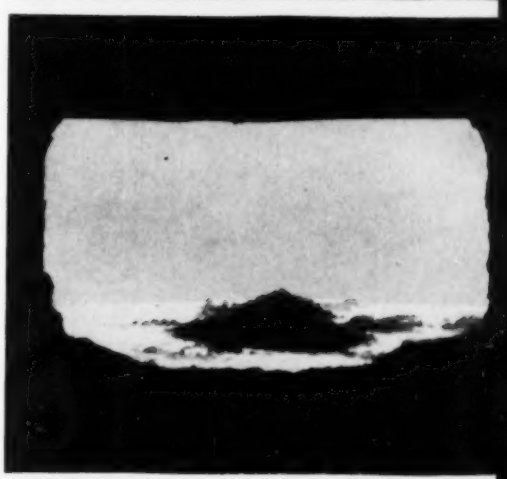
3 FAST SOLUBILITY

A charging machine dumps a loaded box of SIMPLEX ferrochrome in the bath. Because of the speedy solubility of the alloy in pellet form, as much as 15,000 lb. of SIMPLEX ferrochrome can be added to the furnace in one batch.



4 REDUCES FURNACE TIME

The alloy pellets dissolve in the bath more readily than does conventional lump ferrochrome. As much as 45,000 lb. of SIMPLEX pellets can be dissolved in slightly more than one hour. This means reduced furnace time.



5 HIGH METALLIC YIELD

The metallic yield averages about 90 per cent when SIMPLEX ferrochrome is used, since the alloy contains enough silicon to reduce metallic oxides in the slag back into the bath. Overall chromium recoveries of 90 to 95 per cent are obtained regularly.

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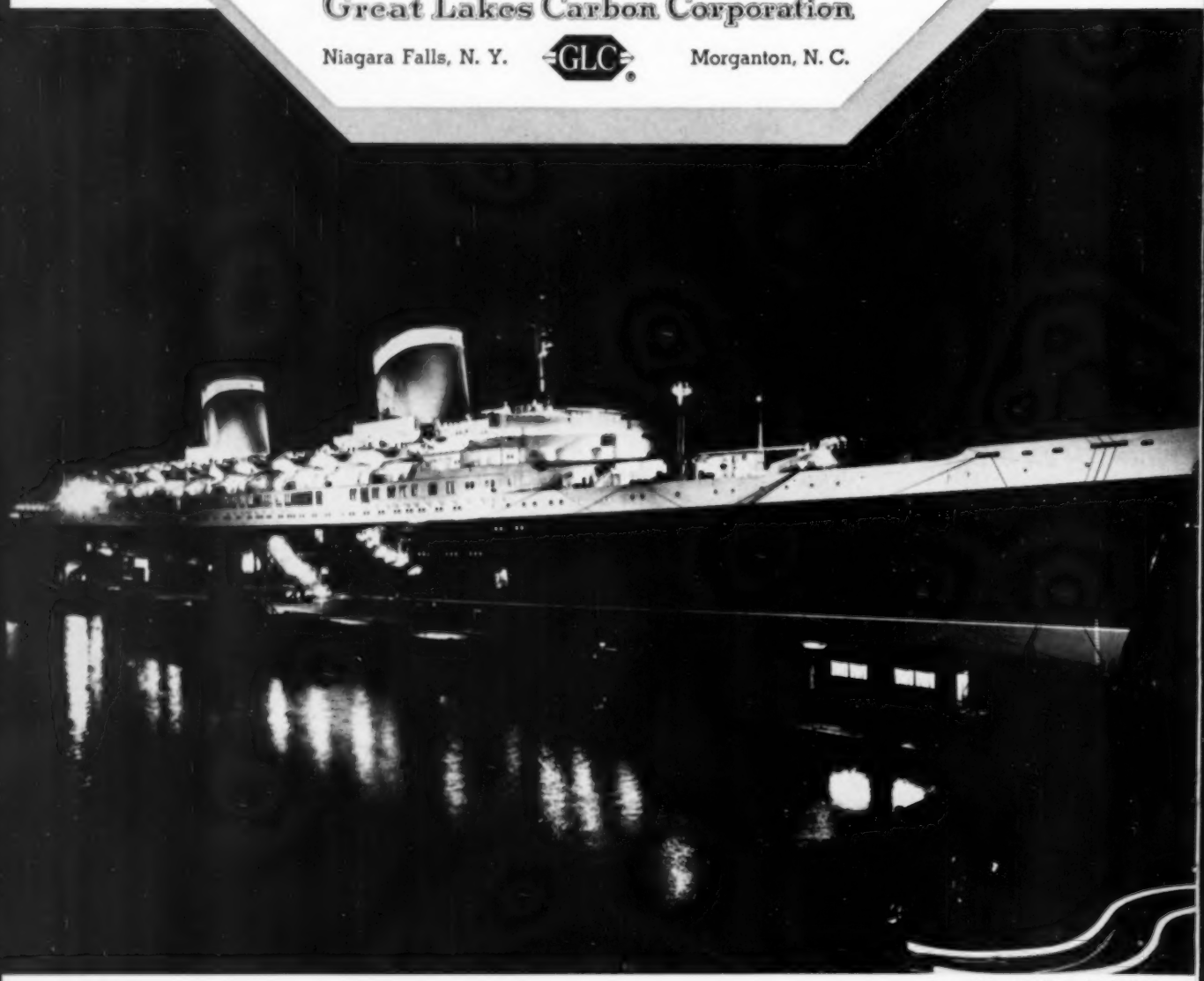

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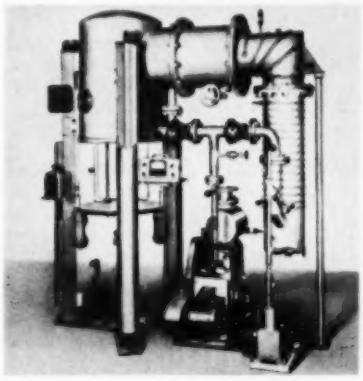
Students are Requested to Apply Directly to Manufacturers for Bulletins and Information

1—CONVEYORS: A new development in metal belt conveyors is announced by *M-H Standards Co.* They carry loads ranging from a few ounces up to 16 tons and will resist wear, heat, cold, high impact, etc. Horizontal conveyors are furnished for both standard and heavy duty applications in widths from 6 to 120 in. and lengths up to 200 ft.

2—VACUUM COATER: High speed pumping system features the *National Research Corp.* rotary gas ballast pump which can pump water vapor without loss of pumping speed



or capacity and without contamination of oil. Model 3111 bridges the gap between experimental work in the laboratory and full-scale commercial production. The vertical coating chamber is 24 in. diam and 30 in. high.

3—BLAST MACHINES: Fast production deburring of soft metal parts, using either a continuous rotating process for small parts or a stationary clamping arrangement for larger units, is possible with two standard Maizo blast machines developed by *Modern Industrial Engineering Co.* A ferris wheel type fixture rotates continuously between two reciprocating blasting guns in model MA-24 at the rate of approximately 1 revolution every 5 min.

4—THERMOBALANCE: New Chevenard thermobalance for the continuous weighing of metals, chemicals or any industrial specimens during a heat treatment or exposure to corrosive influence is announced by *R. Y. Ferner Co., Inc.* One of the most important functions is that it discloses in terms of variation in weight a chemical transformation.

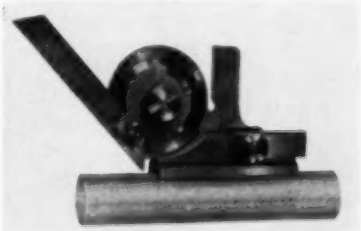
5—FACE SHIELDS: A redesigning of series F200 and F300 face shields by *American Optical Co.* gives $\frac{5}{8}$ in. more clearance between wearer's face and window. Different types and sizes of windows are replaceable and interchangeable on the same headgear.

6—GRAPHITE MOLDS: In order to permit quick deliveries, *National Carbon Co.* has standardized its line of graphite pig ingot molds. These molds are in use as over-metal molds and in casting many special shapes of magnesium, steel, copper, brass and various other metals and alloys quickly and economically.

7—ELECTROPLATING: Development of new methods for volume electroplating of intricate precision components with precision and common metals while holding to closest tolerances has been announced by *American Electro Products, Inc.* The new techniques have proved practical in volume plating intricate components with as many as five electrodeposits controlled to ± tolerances of 0.00001 to 0.000001 in.

8—COATING: *Hanson-Van Winkle-Munning Co.* has announced a new coating for insulating and protecting racks, fixtures, and anode hooks used in electroplating baths. It is unusually tough and ductile. Before coating, a primer is applied to the racks. It is then either brushed, dipped or sprayed on. While still hot they are dipped until thoroughly cooled. Cooling usually takes from 2 to 5 min after the racks have been heated to 350°F for 10 min.

9—VERNIER PROTRACTOR: Stainless steel universal bevel protractor with vernier, features an acute angle attachment for fast setting of fine acute angles. Also, a



new design detachable base keeps the tool in an upright position at all times. *Mercury Supply Co.*

10—INDICATING INSTRUMENTS: Two series of improved portable electric instruments designed for maximum convenience and readability have been announced by *General Electric Co.* DP-11 is designed for general testing for electrical maintenance men who need a rugged easily-read indicating instrument with accuracy of ½ of 1 pct of full scale. DP-12 is a high precision instrument designed for laboratory, field, and production use.

11—RECTIFIERS: Standard unit rectifiers from 3 to 50 kw are now in stock from *American Rectifier Corp.* They are designed for converting ac to dc at the flick of a switch and no warm up period is necessary.

12—SOLARAMIC: A new means of conserving strategic materials and extending metal life at high temperatures through use of a series of ceramic coatings has been announced by *Solar Aircraft Co.*

Free Literature

20—MICROVAC PUMPS: A revised edition of catalog on Microvac pumps for high vacuum has been issued by *F. J. Stokes Machine Co.* Tables of formulas, constants, and conversions frequently used in vacuum processing are included. Useful information on continuous oil purification and other maintenance procedures for high vacuum pumps and solutions to problems of pump selection for typical vacuum systems are given.

21—CU CORROSION RESISTANCE: Results of laboratory research and field study of the nature of corrosive attack on copper and copper alloys have been brought up to date in booklet available from *American Brass Co.* The relative corrosion resistance of the principal types of copper and copper base alloys when in contact with 183 different corroding agents is included in tabular form.

22—HEAT TREAT FURNACES: Installations of gas, oil, and electric heat treating furnaces are shown in brochure obtainable from *Lee Wilson Contracting Co.* More than 14 types of furnaces are illustrated.

23—STAINLESS, MONEL UTENSILS: Catalog illustrating and describing complete line of stainless steel and monel utensils including pails, dippers, funnels, batch cans, and others is available from *Metalsmiths*, div. Orange Roller Bearing Co., Inc.

24—CUTTING FLUID: Applications and methods for use of the new Dynatomics water and oil soluble metal cutting fluid are described in bulletin. Product is said to be suitable for all metal removal operations, including grinding, drilling, boring, etc. *Metalloid Corp.*

25—FORGINGS: Brochure outlining facilities for producing forgings of titanium, aluminum and alloy steels, and sand castings of aluminum and aluminum alloys has been published by *Consolidated Industries, Inc.*

26—PRESSURE GAGES: Types of pressure and vacuum gages used to measure vacuum as great as 10^{-11} mm of mercury and pressures as high as 150,000 psi are described in catalog 7001. Indicators, recorders, pneumatic and electric controllers, and pneumatic transmission are covered. *Minneapolis-Honeywell Regulator Co.*

27—CONTROL INSTRUMENTS: A catalog of control instruments for furnaces, ovens, dryers, and kilns has been published by the *Bristol Co.* A variety of electric, air operated, and electronic control instruments for use with fuel fired and electric heating equipment of all types is listed.

28—UHF: Pamphlet describing *Sylvania Electric Products, Inc.* tubes for UHF has been released. Mechanical and electrical data are described for the various types.

29—FLAW LOCATION: Many applications of *Turco* Dy-Chek are outlined in booklet A-500. It can be used to locate porosity or pin holes in welds, cracks in forgings, grinding cracks in machined parts, etc.

30—HOSE CARE: Bulletin entitled *Tips on Hose Care* may be obtained from *Hewitt-Robins, Inc.* It tells what to do and what not to do in the use and storage of various kinds of hose, including steam, water, and sandblast hose.

31—WIRE THREAD INSERT: Specifications for *Heli-Coil* inserts covering class 2, 2B, 3, and 3B fits are covered in bulletin 652. Uses of wire screw thread inserts in design, production salvage, and maintenance are described.

32—CUT-OFF MACHINES: Folder describes the complete line of cut-off machines. Five models are available for samples from ½ to 3 in. diam. *Buehler Ltd.*

33—VACUUM METALLURGY. Reprint on economical finishing with vacuum metallurgy is available from *National Research Corp.* The use of the process in manufacturing both plastic and metal parts is discussed. Factors that must be considered in determining the applications of this process to specific finishing or coating problems are described.

34—CINDER POTS: Technical bulletin on Johnston corrugated cinder pots has been published by *Mackintosh-Hemphill Co.* The operations performed at the Midland plant to produce cast steel cinder pots having capacities up to 500 cu ft are illustrated and explained. A chronological development of cinder pot design and use is reviewed. Attention is also given to the developments made in recent years.

35—PHASE CONTRAST MICROSCOPY: Theory, practical applications, and equipment used in phase contrast microscopy has been published by *Bausch & Lomb Optical Co.* A bibliography on phase contrast microscopy and related subjects is also included.

36—STEAM CLEANER: Pamphlet issued by *Kelite Products Inc.* describes new oil burning model K15 steam cleaner that fires automatically.

37—GRINDERS: *DoAll Co.'s* line of precision surface grinders for tool room and production grinding operations is described in illustrated catalog. Accessories including grinding wheels, dressing tools, etc., are shown.

38—TITANIUM: *Preliminary Machining Recommendations for Titanium* is the title of booklet published by *Mallory-Sharon Titanium Corp.* It is based on detailed studies of various machining operations.

39—DUCTALLOY: Properties, characteristics, and applications for three standard grades of Ductalloy industrial castings produced by *American Brake Shoe Co.* are described in booklet.

40—FOUNDRY EQUIPMENT: Easy to use guide in selection of oil or gas burners, torches, or heaters for foundrymen is obtainable from *Hauck Mfg. Co.*

41—CALIPER: Stainless steel, rust and tarnish resistant, universal Mauser Vernier caliper for inside, outside, and depth measurements is described in catalog showing complete line of Mauser calipers, height gages, and other equipment obtainable from *George Scherr Co.*

42—COMPLEX ALLOY ANALYSIS: A wall chart showing X-ray analysis curve for a complex alloy (Illium) is available from *North American Philips Co. Inc.* Curve shows peaks for molybdenum, tungsten, copper, nickel, cobalt, iron, manganese, and chromium.

43—METALLOGRAPHY: Test specimens are common metals and alloys mounted and identified, and supplied with photomicrograph, analysis, hardness, etc., for comparison and teaching. *Adolph I. Buehler, Inc.*

44—RAMTITE: Data book issued by *Ramtite Co.* describes methods of construction and maintenance in the various types of steel plant furnaces including all kinds of forge furnaces with Ramtite. Entitled *Steel Plant Furnace Construction with Special Super Ramtite Plastic Refractory*, includes details of application and service results for specific constructions such as burner walls, suspended roofs, etc.

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August

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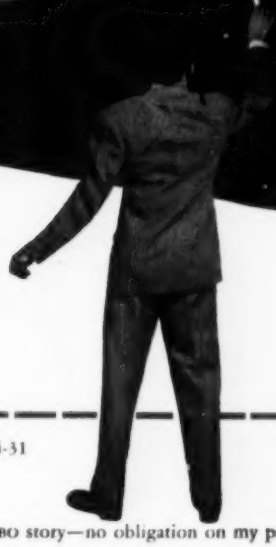

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MEN AVAILABLE

Metallurgist, M.S. degree, British. Four years' nonferrous and ferrous research experience, mainly in the field of high temperature properties of metals, development of creep resistant alloys for gas turbine heat exchanger tubes. Experience in brass tube mill production as piercing, extrusion, drawing. Presently employed with automotive firm; desires position in research, development or production. M-105.

POSITIONS OPEN

Engineers. (a) Senior engineer — metallurgical (#1429), 26 to 35, B.S. in metallurgical engineering, M.S. or Ph.D. degree in metallurgical engineering, with B.S. degree in metallurgy or chemistry desirable. Experience on practical physical metallurgy research and alloy development desirable. Powder metallurgy experience useful. Should have four to ten years' in research and development work or in specialized production. Duties include experimental work toward the development of special parts where metallurgical fabrication is involved or the development of metallic materials. Salary, $5244 to $8172 a year. (b) Senior engineer, mechanical, (#1430), 26 to 40, B.S. in M.E., M.S. or Ph.D. in mechanical engineering with B.S. degree in mechanical or metallurgical engineering desirable. Four to ten years' experience in development or production of small parts assembly, construction and fabrication of small parts. Salary, $5244 to $8172 a year. Location, New York metropolitan area. Y8827.

Chemical or Metallurgical Engineer for laboratory and pilot plant operations covering development of nickel cadmium battery. Must be citizen. Salary, $4080 to $4920 a year. Location, Westchester County, N. Y. Y8811.

Assistant metallurgist with college degree in metallurgy, preferably a recent graduate, with background in physical metallurgy. Some of the work will be on nonferrous alloys. Will be expected to investigate methods of fabricating metal parts including actual working, heat treating and joining of metals. Problems in ferrous metal fabrication and heat treatment will be encountered. Work in the powdered metal field will also be covered to some extent. Salary about $3900 a year depending on applicant. Location, Massachusetts. Y8808.

Sales engineer, young, graduate, mechanical, with several years' sales experience, preferably in the metals field, i.e., knowledge of piping, tubing and tanks as used in the petroleum and chemical industries. Salary, $7200 a year plus bonus. Location, Detroit, Mich. Y8794.

Instructor or Assistant Professor with doctorate degree, with some industrial experience, to teach both graduate and undergraduate course in physical metallurgy. Opportunity to do consulting or other work during the summer, and also during the school year, if it does not interfere with class work. Rank and salary open. Location, Southwest. Y8753.

Standards Engineer, E.E. or metallurgy graduate, with at least two years' materials testing and standards specifications covering electronic and metallurgical components. Salary, $4420 to $6500 a year. Location, eastern Maryland. Y8750(b).

Engineers. (a) Welding engineer experienced in welding stainless steel and nonferrous metals. Will do all the engineering in connection with new modern brass foundry, and solve technical problems. Salary up to $7500 a year. (b) Foundry engineer for brass foundry work. Salary, $6000 to $7000 a year. Location, South. Y8715.

Metallurgist with Master's degree or equivalent, to be responsible for the preparation and treatment of alloys used for basic investigations on metals. Work involves such techniques as vacuum and arc melting, handling of rare metals and vacuum annealing. Location, Illinois. Y8424.

An editorial position is open for a metallurgical engineer on the AIME editorial staff in New York. Some operating background and editorial experience desirable. Write: E. H. Robie, Secretary, AIME, 29 W. 39th St., New York 18.

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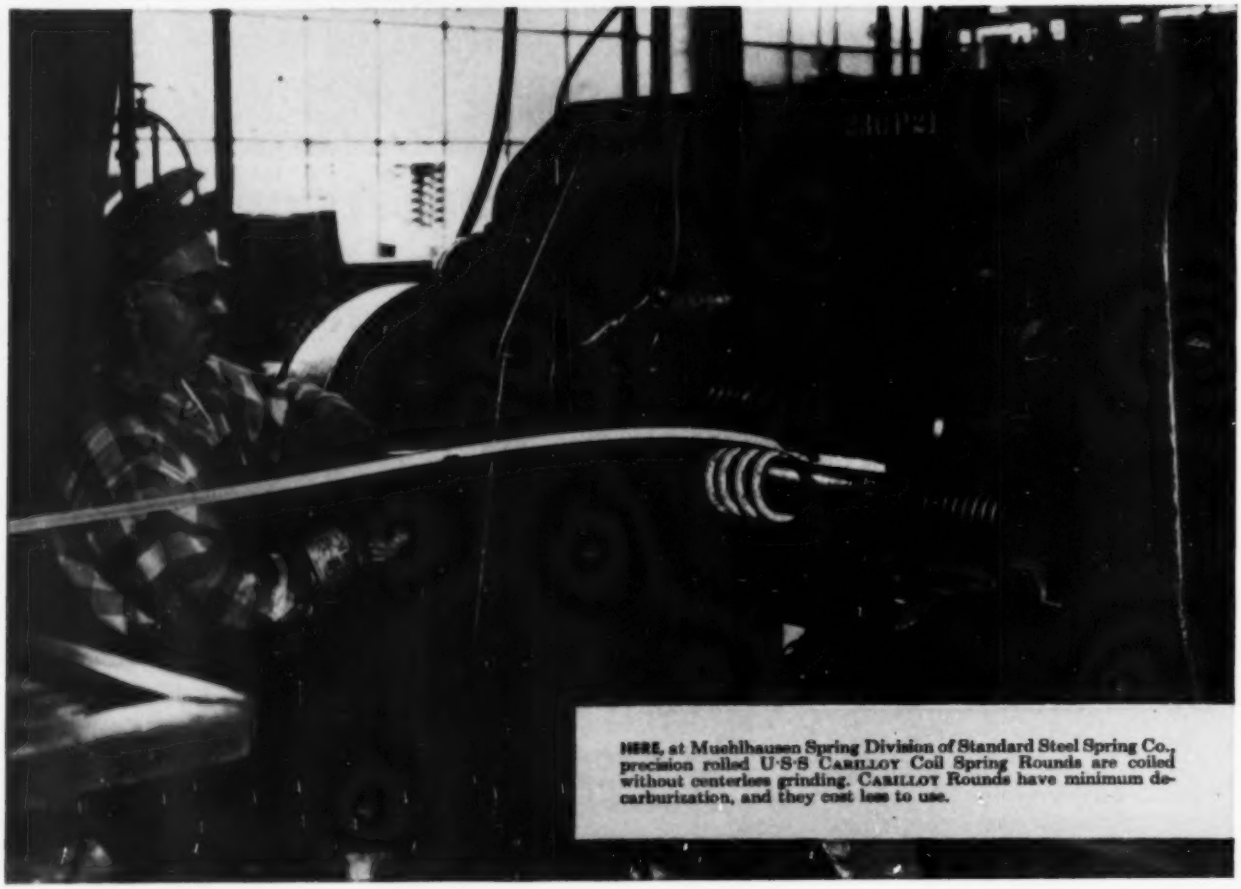

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IN the early days of the development of coil springs for front suspensions of automobiles, the only steel that was available was an ordinary hot-rolled bar from which as much as .035" of metal per side had to be removed by grinding to insure freedom from harmful seams, pits, and decarburization. This cost money, was wasteful and time consuming.

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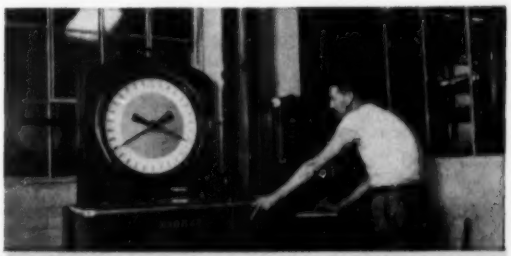
Our experienced engineers and metallurgists will be glad to consult with *you* on any steel or fabrication problem. Just write to United States Steel, 525 William Penn Place, Pittsburgh 30, Pennsylvania.



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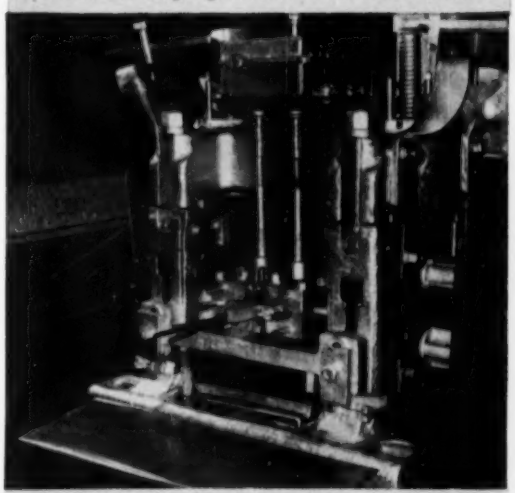

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Coming Events

Aug. 17-19, Society of Automotive Engineers, international west coast meeting, Vancouver, B. C.

Aug. 19-21, Western Electronic Show and Convention, San Francisco.

Sept. 11, AIME, St. Louis Local Section, Lead Belt Meeting, tour St. Joseph mines and mills.

Sept. 13-16, Electrochemical Chemical Society, Inc., Ocean Terrace Hotel, Wrightsville Beach, N. C.

Sept. 14-17, Society of Automotive Engineers, tractor and production forum, Milwaukee.

Sept. 16-18, Porcelain Enamel Institute, annual shop practice forum, Columbus.

Sept. 17-18, National Foundry Assn., annual meeting, New York.

Sept. 19, AIME, National Open Hearth Steel Committee, Chicago Section, golf party.

Sept. 21, ASME, Industrial Instruments and Regulators Div., and Instrument Society of America, exhibit and joint conference, Sherman Hotel, Chicago.

Sept. 21-22, Steel Founders' Society, fall meeting, Hot Springs, Va.

Sept. 21-23, American Mining Congress, Metal and Nonmetallic Mineral Mining Convention, Olympic Hotel, Seattle.

Sept. 28-30, National Electronic Conference, Chicago.

Sept. 28-30, ASME, Petroleum Mechanical Engineering Conference, Rice Hotel, Houston.

Oct. 5-7, ASME, fall meeting, Hotel Sheraton, Rochester.

Oct. 6, AIME, National Open Hearth Steel Committee, Buffalo Section.

Oct. 7, AIME, National Open Hearth Steel Committee, Chicago Section, Phil Smidt's, Chicago.

Oct. 7-9, National Assn. of Consulting Engineers, south central region, Mayo Hotel, Tulsa, Okla.

Oct. 8-9, National Conference on Industrial Hydraulics, annual meeting, Hotel Sheraton, Chicago.

Oct. 9, AIME, St. Louis Local Section, St. Louis University, St. Louis, Mo.

Oct. 9, AIME, National Open Hearth Steel Committee, Eastern Section, fall meeting, Warwick Hotel, Philadelphia.

Oct. 15-17, AIME, National Open Hearth Steel Committee, Southwestern Section, fall meeting, Baker Hotel, Dallas, Texas.

Oct. 19-21, AIME, Institute of Metals Div., fall meeting, Hotel Allerton, Cleveland.

Oct. 19-23, National Metal Congress and Exhibition, Cleveland.

Oct. 22, AIME, St. Louis Local Section, Engineers Club of St. Louis and ASCE, Engineers Club, St. Louis.

Oct. 27, Assn. of Consulting Chemists & Chemical Engineers, 25th anniversary annual meeting, Hotel Belmont Plaza, New York.

Oct. 28-31, AIME, El Paso Fall meeting, El Paso.

Oct. 29-30, AIME Coal Div., ASME Fuels Div., Conrad Hilton Hotel, Chicago.

Oct. 29-31, National Council of State Board of Engineering Examiners, Annual Meeting, Plaza Hotel, San Antonio, Texas.

Oct. 30-31, AIME, National Open Hearth Steel Committee, Deshler-Wallick, Columbus.

Nov. 4-6, Time and Motion Study and Management Clinic, Sheraton Hotel, Chicago.

Nov. 5-7, Electron Microscope Society of America, annual meeting, Pocono Manor Inn, Pocono Manor, Pa.

Nov. 6, AIME, National Open Hearth Steel Committee, Pittsburgh Section, William Penn Hotel, Pittsburgh.

Nov. 13, AIME, St. Louis Section, coal meeting, York Hotel, St. Louis.

Nov. 29-Dec. 4, ASME, annual meeting, Statler Hotel, New York.

Nov. 30-Dec. 5, Exposition of Chemical Industries, Commercial Museum and Convention Hall, Philadelphia.

Dec. 2-4, AIME, Electric Furnace Steel Conference, Netherland-Plaza Hotel, Cincinnati.

Dec. 11, AIME, St. Louis Section, York Hotel, St. Louis.

Dec. 13-16, American Institute of Chemical Engineers, annual meeting, Hotel Jefferson, St. Louis.

Dec. 28-29, Annual Chemical Engineering Symposium, University of Michigan, Ann Arbor.

Feb. 15-18, 1954, AIME, annual meeting. Metals Branch, Hotel McAlpin; Mining and Petroleum Branches, Hotel Statler, New York.

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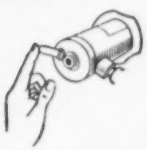

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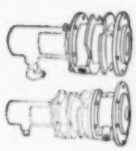

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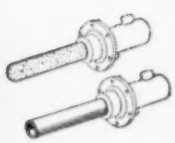

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Aluminum in Iron and Steel, by Samuel L. Case and Kent R. Van Horn. *For the Engineering Foundation by John Wiley & Sons.* $8.50, 478 pp., 1953.—This book is the first of a new series of Alloys of Iron Monographs. First part contains a summary of data showing the favorable affect of small amounts of aluminum when added to molten steel as a deoxidizer. The second part is a correlation of data on the effect of aluminum as an alloying element in steel. Extensive treatment is given to the phenomena of inclusion formation, grain size, notch sensitivity, and aging. Material for the book was drawn from more than 340 sources.

Ferrous Analysis, second edition by E. C. Pigott. *John Wiley & Sons,* $12.50, 690 pp., 1953.—The author has remodelled the book and prepared additional material. Detailed treatment of methods of determining hydrogen, nitrogen, and oxygen has been added in answer to a general demand made by reviewers. As in the first edition, the aim has been to conform to practical requirements by providing methods that will fall within the scope of the average laboratory, and that are reliably selective and accurate, rapid and economical, and of general application.

Low Temperature Physics, by Charles F. Squire. *McGraw-Hill Book Co.,* $6.50, 224 pp., 1953.—The text offers descriptions of matter at extremely low temperatures, together with experimental results which show obedience of these properties to quantum laws. Excellent background is furnished for the understanding of current papers on low temperature physics and chemistry. The book includes many important unsolved problems of a fundamental nature, especially in relation to superfluid helium and superconductivity. Most of the material is new, having appeared since the end of World War II.

Gases in Metals, by D. P. Smith, L. W. Eastwood, D. J. Carney, and C. E. Sims. *American Society for Metals.* $3.00, 204 pp., 1953.—Four lectures cover fundamental metallurgical and thermodynamic principles of gas-metal behavior, gases in nonferrous metals and alloys, gases in liquid iron and steel, and behavior of phases in solid steel and iron. A bibliography accompanies each article.

Historical Metrology, by A. E. Berriman. *E. P. Dutton & Co.* $3.75, 1953.—New light is thrown on the historical aspect of metrology—the 'ology of weights and measures. For the general reader contact is provided with some of the leading personalities of the ancient world. For the archaeologist and the numismatist there are tables in which the principal ancient standards of length and mass are given precise values. Historical links are established with metrological standards of the past.

Annual Review of Nuclear Science, Vol. II. *Annual Reviews Inc.* $6.00, 429 pp., 1953.—Sixteen topics, including the following are covered in this review: Origin and distribution of the elements, production and distribution of natural radiocarbon, recent progress in accelerators, nuclear and photonuclear reactions, subnuclear particles, radiation effects in solids, isotopes, nuclear moments, cosmic rays, and high energy fission.

Behavior of Metals at Low Temperatures, by R. M. Brick, J. R. Low, Jr., and C. H. Lorig. *American Society for Metals,* $3.00, 112 pp., 1953.—The book is a reprint of three lectures: Behavior of Single Crystals and of Pure Metals, dealing primarily with mechanical properties and basic related phenomena; The Influence of Mechanical Variables, considering the effect of stress-state, rate of loading and other topics on strength and ductility; and Influence of Metallurgical Factors, mainly concerned with ductility and brittle fracture susceptibility.

Zirconium and Zirconium Alloys. *American Society for Metals.* $7.00, 354 pp., 1953.—Twenty one papers in this book constitute a symposium covering: Zirconium ores and extractive metallurgy processes, preparation of zirconium powder, manufacture of zirconium sponge, fabrication of zirconium, metallographic procedures, and corrosion resistance. Several papers cover investigation of various zirconium binary systems, with emphasis on phase diagrams. The last paper discusses zirconium with relation to nuclear reactors.

Engineers as Writers, edited by Walter J. Miller and Leo E. A. Saidla. *D. Van Nostrand Co., Inc.* $4.25, 340 pp., 1953.—This is a text in technical composition. Selections from the works of 15 engineering writers are presented with a critical analysis following each selection. Suggestions for study and topics for oral or written reports are included. Though most of the selections are easily understood by the laymen a few highly technical writings are included.

Review of Current Research and Directory of Member Institutions. *Engineering College Research Council of the American Society for Engineering Education.* $2.50, 330 pp., 1953.—An attempt has been made through this publication to give as accurately as possible a picture of all research programs at all member colleges. An attempt has been made to separate vigorous research programs on a single topic from that of the individual work of a person interested only in intellectual satisfaction. Figures on finance and manpower, as available are used to supply some evidence of the situation. The publishers point out, however, that in this day of monumental scientific growth, results cannot be considered a final accounting.

Principles of Heat Treatment, by M. A. Grossmann. *American Society for Metals,* $5.00, 303 pp., 1953.—This is a revised edition of an original series of lectures covering principles of hardening, hardenability and quenching, surface hardening, transformations during cooling, normalizing and annealing, grain size considerations, and determination of transformation diagrams. Fundamentals are emphasized, and a clear, logical approach is used.

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Industrial Notes

• Additional equipment at Chrysler Corp.'s Amplex plant in Detroit has increased facilities for production of Oilite stainless steel products pressed from metal powder. One of the products now in volume production is an exhaust manifold heat control valve bearing. The valve bearings are said to be more corrosion resistant than bronze, and have a 40,000 psi tensile strength.

• One week after a tornado smashed into Worcester, Mass., the new Norton Co. grinding machine plant began a period of rehabilitation after suffering estimated damages of more than $1 million. The roof is almost completely closed in and machines are busy on the production line. One office paper, a change order, was reclaimed some 35 miles from the plant, on the front lawn of U. S. Senator Leverett Saltonstall.

• Pneumatic tubes at the Roebling, N. J. steel mill of the John A. Roebling's Sons Corp., race open hearth steel samples from furnace to laboratory at a speed faster than the average man can run. The samples travel a distance of one tenth of a mile in about 20 sec. The system permits more frequent quality control tests. While the pneumatic tube is not the first used in a steel plant it is believed to be the first used in a closely integrated operation such as Roebling's.

• Kaiser Engineers established an atomic energy div. for exploration of various approaches to industrial use of atomic energy, including power and radioactive byproducts. J. H. Hayner, formerly of the Atomic Energy Commission, has been appointed division manager.

• A contract has been signed by Applied Research Laboratories of Glendale, Calif., manufacturers of spectrochemical equipment for testing inorganic and organic materials, for production of what has been termed a revolutionary tin plate thickness gage for Jones & Laughlin Steel Corp. The instrument, engineered by J&L, uses the X-ray principle for measurement of thickness of tin on steel to accuracies of 0.000001 in. Measurements are made automatically while the tin plate is traveling at high speeds as a continuous sheet. The contract calls for delivery of three instruments by early 1954.

• Lake Erie Engineering Corp. is building four cold extrusion presses for use in civilian production at the Mullins Mfg. Co. plant in Warren, Ohio. Lake Erie Engineers have built about 25 of the hydraulic presses for steel extrusion since 1949. Presses made for Mullins by Lake Erie weigh 700,000 lb and exert 3000 lb pressure.

• Republic Steel Corp. announced that it will build a plant at Toledo, Ohio, using its new process for making powdered iron. Initial capacity will be 50,000 lb per day. The process is the result of the company's research for an economical way of direct reduction of iron ore to high purity iron, bypassing certain conventional smelting steps. The new plant will be built on property near the Toledo refinery of Sun Oil Co., which expects to complete new facilities for high octane gas production by October. Hydrogen, a byproduct of the oil concern's operations, is necessary for the new powdered iron process.

• Mangaslag, Inc. installed three 30-ton kilns at its plant at Coxton Yards, in the Wilkes Barre, Pa., area. Vulcan Iron Works of Wilkes-Barre manufactured the kilns. Production is expected about August 1, with some 100 men employed in ferromanganese production.

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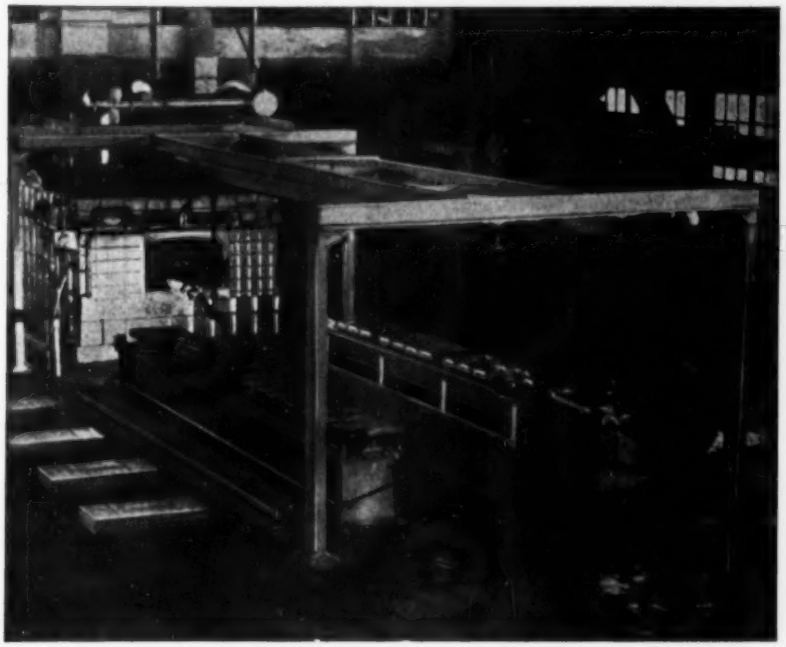

Low frequency induction furnace for melting of zinc.
Melting capacity: 80-110 tons per 24 hours
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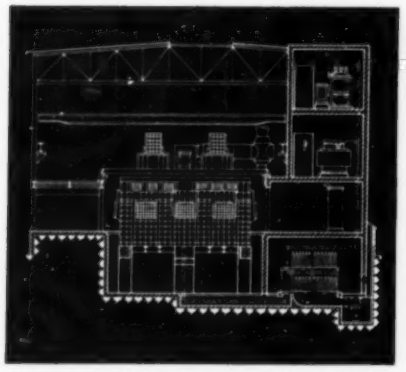

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Colorado Fuel & Iron Corp.'s Petit char plant is believed to be the second of its kind in the world. It's actually a low temperature furnace.

COLORADO Fuel & Iron Corp.'s new pilot plant for test production of char may be another step forward in rectifying the inequalities of nature. The plant is designed to make Colorado coal age several million years in matter of minutes. Colorado coal is something like 80 million years younger than eastern coal. Because of its immaturity it is highly volatile.

The new char plant at CF&I's fully integrated steel mill at Pueblo is really a low temperature furnace which removes part of the excess volatile matter. It produces a low volatile coal or char which can be blended with other coals. Mixing the resultant char with Colorado coking coals improves the quality of the coke.

In the Petit process char plant two gas burners feed 2500 ft per hr of flaming gas into a vertical chamber zig-zagging 50 ft down the center of the tower, where a steady flow of coal is converted into char. About 1 ton of coal per hr is handled by the furnace to produce 1600 lb of char. With the construction of the plant the value of improving western coal can be established over a period of time. CF&I engineers started work on the plant in January of this year, with the Koppers Construction Co. of Pittsburgh. Construction was based on plans of the Societe de Technique Industrielle of Paris. The final test of the value of char blending will be use of the material in coke ovens and blast furnaces.

An experimental Hayes retort was built near the present Petit plant in 1942. Results of this earlier work by CF&I played an important part in the development of the char theory and some parts of the old plant were used in construction of the new one.

A. F. Franz, CF&I president, feels that "it is too early to estimate the effect this char plant will have on CF&I's future steel production but completion of the pilot char plant is a significant step in our long range plan to utilize fully the steelmaking resources available to us locally.

"Development of our new Allen mine in southern Colorado, with its intensive mechanization and latest type belt conveyor systems, earlier this year, represented a major step in this program. Large reserves of coking coal have been one of the important factors in the continued program of expansion and modernization of Pueblo mill. Completion of the pilot char plant is merely another part of our continuing search for the best possible use of this vital resource."

The char process dates back to 1908, when Kotara Shimomura of Japan was one of the first to develop the theory of mixing char with high volatile coal. The Daniel Petit process represents one of the more advanced approaches.

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LUKENS Steel Co. has released a new nontechnical film on how clad steel equipment is aiding industry to receive new profits in the $130 billion a year consumer goods market. Recently, Lukens developed a process for manufacturing aluminum clad plates and intends to continue studies on clad steels made with scarce and high priced metals such as tantalum and zirconium. If successful, these scarce metals may be made to go much farther than current supply allows.

In the film, the versatility of clad steel plates is described. Uses of these more economical bimetals is explained in simple terms understandable to the layman. Tonnage sales for bimetals have jumped some 2000 pct since 1939.

At the firm's Coatesville plant, the world's largest continuous heat treating furnace for steel plates is under construction. The 365 ft unit is the center around which the alloy finishing plant is being constructed. It will provide heat treatment up to 1950°F, about 400°F higher than conventional units used for treating plates.

G. Donald Spackman, vice-president in charge of operations, pointed out that "it used to take 27 interplant transfers to make clad steel plates and material had to be moved over 10 miles. Now there are only 13 interplant transfers, and the distance traveled has been reduced to 4 miles."

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THE first Basic Materials Conference held concurrently with the first Exposition of Basic Materials, at New York City, proved to be of great interest to executives, scientists and practical operating men. Leading thinkers and practitioners of the metallurgical engineering profession were on hand and several of them participated actively. Francis B. Foley, consulting metallurgist, Bayonne research laboratory, International Nickel Co., Inc., Bayonne, N. J., discussed *Materials for Low Temperature Service*. After stating some of the more general facts concerned with this particular field, he delved into more specific research problems. Mr. Foley pre-

sented some of knowledge gained on this frontier of materials applications.

New Material Developments, presented by Julius J. Harwood, assistant head, metallurgy branch, Office of Naval Research, Dept. of the Navy, Washington, D. C., noted that for the next several years practically all titanium production will be used for military applications. "The military requirements for 1954 have been announced as 25,000 tons, and there is some possibility that this figure may be increased." Mr. Harwood pointed to the wide field of materials available to the engineer, while giving an account of the progress on the frontiers of material development.

Considerable interest was generated by a new nickel plating process exhibited by General American Transportation Corp. The company is building two plants, one at East Chicago, Ind., and the other at Los Angeles, which will utilize the process, called Kanigen.

No electrolytic equipment is required in the process and according to the reports the process stretches the available nickel supply. With Kanigen, it becomes possible to plate almost any solid substance with a predictable thickness of nonporous plate. According to the company the process proved satisfactory for production line plating of steel, copper, brass, bronze, stainless steel, and aluminum. It is estimated that equivalent plate protection can be obtained with one third to one half the nickel required by other processes.

General American originally established a plating research program in search of a method to protect the insides of its tank cars, which carry corrosive chemicals and materials. The Kanigen process was developed through reduction of nickel by use of hypophosphites.

Kanigen plate is a nickel-nickel phosphide composition. Normally it runs about 5 to 8 pct phosphorus and has a Vickers hardness of 550 to 650. The company states that thickness can be controlled to within 0.0001 in.

Properties claimed for the Kanigen process are: throwing power, 100 pct; uniformity of coating; excellent adhesion; good corrosion resistance of basis metal; and virtually no pores.

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A new melting process has been announced for production of titanium ingots reported to have characteristics superior to anything presently known, and in addition increases the yield of metallic titanium from its sponge raw material. Arc melting and induction melting, the standard methods employed by various producers, have their advantages and disadvantages.

Mallory-Sharon Titanium Corp., in announcing the new method, claims that the best features of the two processes have been combined. Results of initial production have reportedly exceeded the most optimistic hopes of engineers and metallurgists. Method *S*, as the process is called, offers ingots which are homogeneous and displays the same characteristics throughout. Ingots of a given type are reproducible and size and shape can be varied over a wide range. Carbon content can be controlled to a specified amount and held as low as the amount inherent in the sponge material. A titanium electrode is used in place of a carbon electrode, and melting is done in a water-cooled copper crucible. Yield is greatly increased and more titanium metal is realized from a given amount of sponge raw material since scrap loss is reduced. The new process is flexible and can be used for a wide range of alloys. Mallory-Sharon is devoting most of its production to its MST Grade III light gage rolled sheet, but production of MST 3 Al-5 Cr alloy is on the increase. With a tensile strength of about 165,000 psi its controlled carbon content, via the new process, should make it even more desirable.

Mallory Sharon Titanium Corp. can control carbon content of titanium sponge in the manufacture of titanium ingots. Titanium ingot made by the new process and dumped from crucible is highly homogeneous.

BERYLLIUM Corp. is planning to investigate other materials with an aim to diversification. The firm also is planning an extensive modernization program. On order is a specially designed hydraulic extrusion press, expected to cost about $365,000. The unit will produce alloys in the form of rod, special shapes, wire, structural sections, and beryllium alloy tubing.

A Sendzimer mill to roll strip up to 11½ in. in width at speeds up to 200 ft per min, is also on order. Estimated commitments for capital additions yet to be delivered is about $500,000. A 4000-lb furnace for casting ingots is also on the schedule at a cost of $73,000.

Beryllium Corp. is currently investigating methods for increasing the oxide yield from beryl ore, improved techniques for manufacture of beryllium alloys, and development of alloys of low beryllium content.

New materials, such as ferroberyllium as an additive to certain steels, are on the program. Another field of investigation is alloys containing no beryllium but having some properties akin to beryllium alloy systems.

12% increase in production over other natural draft furnaces in the mill

11% decrease in fuel burned per ton

. . . that is the 2-year record of this Morgan-Isley controlled open hearth at the Alan Wood Steel Company

The open hearth has a 125-ton capacity, burns up to 500 gallons of oil per hour operating on a hot charge. Primary and extra large secondary checkers (permitted by Morgan-Isley design) trap most of the heat. The flue gas enters the base of the secondary regenerators at about 1600°F. The stack temperature averages about 750°F. The low stack temperature and the exceptionally large heat storage result in the tonnage increase and fuel saving shown above.

Let us tell you more about Morgan-Isley.

MORGAN CONSTRUCTION COMPANY WORCESTER, MASS.

ROLLING MILLS • MORGOIL BEARINGS • REGENERATIVE FURNACE CONTROLS • EJECTORS • PRODUCER GAS MACHINES

PITTSBURGH, PA., 2815 Koppers Bldg. *English Rep.*, International Construction Co., 56 Kingsway, London W. C. 2, England

Drift of Things

IN an editorial "Discoveries Yet To Come," *The New York Times* reported on a meeting of 75 outstanding scientists, engineers, and businessmen at which Ralph J. Cordiner, president of General Electric Co. "pleaded for more fundamental research by industrial laboratories and supported his argument with the announcement that his own company planned to increase its research staff from 1000 to 1500."

General Electric is one of the companies whose existence and position today is based on research. Not content with developing a product, and continuing to market it, the company works continuously on new developments with an eye to the future. The scope of operations also has been extended by this means, and the variety of products marketed today is a far cry from the early days of its existence.

Alert organizations recognize the importance of engineering societies in helping to advance the technology and the individual. The various professional societies act as a clearing house for bringing together engineers and providing them with the opportunity to present their findings to other engineers.

The *General Electric Review*, a publication of the General Electric Co. is currently running a series on Engineering Societies of America. The July issue contained the story of AIME, written by our Secretary, Ed Robie. We don't understand how he found time to prepare this material, for the boiling down of the early history, organization, publications, meetings, awards, and membership details of the Institute into 3 pages must have been quite an undertaking. The editor of the *General Electric Review* is to be congratulated for having conceived the idea of a series of this type. It is a service to all of the Review readers.

The societies located in the Engineering Building in New York, constituting the hub of technical professional societies—AIME, ASCE, ASME, SAE, AIEE—with AIChE have taken additional steps among themselves to improve their methods and services. Under an informal arrangement, there are meetings of staff members of the various societies under activity groups—publications, membership, meetings, etc. In this way there is continuous interchange of information on methods, projects, and new ideas among the groups involved. We like to think that the business of conducting a technical society is a profession in itself, and the informal group formed is a professional society within a professional society.

A PATENT was issued not too long ago to two Japanese inventors, one of whom coauthored a paper in the January 1952 issue of JOURNAL OF METALS, for a method of making "metallic articles reserving perfume in their own structure and emanating fragrance." The method is basically that of impregnating a porous powder metal part with perfume. The inventors mention that although jewelry and art objects would be the principal applications, it could find use for fragrant signboards. Also, "such a fragrance-emanating device may be fitted to a part of radio instruments or piano or any other organ so that fragrant utensils may be obtained." This now opens unlimited possibilities.

Fragrant signboards may be the solution to many a motoring problem. Driving along of a hot summer day, gently wafted odors of say Chanel No. 5 would do much to rid the air of exhaust fumes, especially from the diesel truck or bus that always seems to be ahead. The ride would be more pleasant, and the soothing influence would do much to defray tempers.

Then too, in the home, one excellent application might be in television sets. Although television was not specifically mentioned along with radio, we attribute this to the lack of television facilities in Japan. There is many a television commercial, and unfortunately many a television program, whose odor could be immediately detected upon tuning in the station, thus obviating several minutes of frustrated viewing. The day seems not too far off when one can pass a neighbor's house and be able to determine the programs they are listening to or watching, as well as what is cooking—for dinner, that is.

MANY European engineers have been visiting the United States in the last year or two, and some of them have written up their impressions. Among these is Edmond Hianné, who has kindly supplied us with a mimeographed copy of a lecture which he delivered after his return. Therein he says that "in New York, the Engineering Societies have united their efforts and that, between them, they own a skyscraper, the Engineering Building, . . ." Now it had never occurred to us that we worked in a skyscraper; apparently a sixteen-story building seems pretty tall to a European engineer. It does not scrape much of the sky in New York, however. Right in the same block with us, there is a higher building to the north, east, and west. Only to the south can we have an unbroken look for perhaps a quarter of a mile—to the Empire State Building on 34th Street, which has 102 stories, and is 1472 ft high—the tallest building in the world.—E.H.R.

JAMES T. KEMP, American Brass Co., sent us some light reading matter. It was an article by R. P. Lister, in a recent issue of the famous *Punch*, entitled "The Truth About Creep." In a manner that can best be described as light and intelligent, Lister discusses his experience with creep, and jet engine production. In frivolous manner, he relates how he always wanted to determine the exact point in a gas turbine engine at which it stops sucking air and starts to blow it. He closes his discourse on turbine blades with:

"I am not, of course, in a position to disclose any details of the performance and characteristics of the materials used, but I am glad to be able to inform the public that the use of lead and its alloys for gas-turbine blades has been entirely discontinued. We have never even tried pitch."

We enjoy literature of this type, our favorite nontechnical magazine being *The New Yorker*. However, we have found that engineers and scientists contribute few articles and books to nontechnical literature. We hesitate to say that technical people here do not have the broad interests that would make this possible. They are just not proficient in that kind of writing. If they were, we feel confident that the public would be receptive.

Alvin S. Cohan

One of the Largest single acting engines in service east of the Mississippi. Built at the Hamilton, Ohio plant of BALDWIN-LIMA-HAMILTON CORPORATION, it is a straight 12 cylinder Diesel engine running on crude oil. With DEMA stationary standard equipment, its shipping weight is 485,000 pounds.

Nickel Alloys Help build stamina into an Engine that serves a city

Built to handle the main power load for the city of Decatur, Indiana, this unit shows how nickel alloyed steels and irons are used in advanced design for increased power, quieter operation and longer trouble-free life.

Its forged crankshaft gear ... specified in Type 4340 or 9845 nickel alloyed steel ... provides:

Tensile strength	140,000 psi minimum
Yield Strength	118,000 psi
Elongation	16%
Reduction in area	45%
Brinell hardness	280 to 310

Piston heads are cast in high strength nickel-chromium iron to withstand heat stresses. Cylinder liners are one-piece castings containing .50% to .75% nickel and .25% molybdenum, for resistance to both heat and wear. Carburized nickel-molybdenum steel, Type 4615, is ordinarily specified for cams and rollers, and wrist pins are of Type 8620 nickel-chromium-molybdenum steel.

Consult us on the advantages of nickel in your products or equipment. Send us details of your applications for our suggestions.

Ductile Iron Gas Valve Bodies for HAMILTON Diesel engines undergo an 800-pound pressure test prior to assembly. Steel jackets are welded to these bodies with Ni-Rod 55. The castings are stress relieved for four hours, at 1200°F., and placed in service at 240 BHN. The Ductile Iron bodies prove sounder than those of cast steel, are easier to machine, and combine ample strength and ductility to withstand sudden pressure overloads.

At the present time, nickel is available for end uses in defense and defense supporting industries. The remainder of the supply is available for some civilian applications and governmental stockpiling.

EMBLEM OF INCO SERVICE

THE INTERNATIONAL NICKEL COMPANY, INC. 67 WALL STREET NEW YORK 5, N. Y.

Interest is growing in ion exchange for metal recovery. In uranium recovery at one South African plant, cyanide tailing is leached and the solution passed through purifiers where iron, aluminum, and silica are precipitated. The solution is subject to ion exchange, presumably to enrich the liquor and uranium recovered as the oxide. Hydrometallurgical applications of ion exchange are discussed in this month's JOURNAL OF METALS, p. 980.

The Schaaber Dilatometer used in salt bath heating processes offers speedier determinations of transformation time for austempering, according to Ajax Electric Co., who tested this new German device. In addition, the device makes martempering time cycles available before transformation begins and determines the severity of the quenching medium. It also serves as a control check for steels prior to processing. Principle of operation is based on the volume change which takes place in transformation of austenite.

Chrysler Corp., Amplex div., has been using powder metal for rotating bands on 90 mm ammunition. The use of oilite iron rotating bands is said to add to the effectiveness of the shell in addition to saving tons of strategic metal. Bands were originally made of copper and gilding metal. The oilite metal powder bands are porous and soak up lubricant which oozes out under heat or pressure in the gun barrel.

Only six items remain on the scarce material list of the National Production Authority. They are: Diamond grinding wheels, chromium, cobalt, columbium-tantalum, molybdenum, and nickel.

The U. S. Air Force heavy press program has been slashed. Original plans called for 17 presses to be built. Air Force directives have not been clear as to the exact status of some of the presses under construction. First cut announced dropped 7 of the units, but since then modification of the order has been reported.

A slow down on disposal of Government stocks of zinc has been decided upon by the British Ministry of Supply. Following termination July 31, of the provisional disposal plan, all metal from remaining stocks will be sold at the rate of 2000 tons per month, compared with 4000 tons monthly and other sales by the Government's metal broker. Stocks in the hands of the Government after July 31 will be an estimated 64,000 tons. It will take almost three years to sell. The announcement was not provocative of market change.

Unofficial estimate of steel production for the first six months of 1953 is around 53 million tons. Figures are based on weekly operating rates. Concensus of opinion concerning remainder of the year is that production will fall off slightly. Vacations and repair shutdowns are expected to cut into summer output.

Fig. 1—Aerial view of U. S. Steel's Fairless works under construction, shows the giant steel plant rapidly taking shape.

Design Features of Fairless Works Open Hearth

by H. A. Parker

THE nine stationary basic furnaces comprising the Fairless works open hearth, constructed in the interest of national defense, are the most modern and among the largest furnaces operating on a hot metal charge. Although not phenomenally different from other open hearths, there are features of the furnaces that should interest operators, and others in the steel industry. Some basic principles of open hearth design and operation given particular emphasis were: Generous hearth area and regenerator volume; rapid charging and flushing; and speedy furnace rebuilding and patching.

The furnaces are spaced on 117-ft centers with approximately 20 ft between them. The charging floor proper extends two bays, 117 ft north of No. 1 furnace. There are four additional bays, 234 ft of partial floor enclosing the hot metal transfer station. The charging floor and building extend one bay south of No. 9 furnace and there is an additional level trestle area of two bays beyond this.

Hearth

Of primary consideration is the hearth itself. The first discussion will be that portion of the furnace above charging floor level.

The hearth at top of hearth casting or sill level, is 60 ft long x 18 ft 6 in. wide, measured inside the brickwork. This gives a hearth area of 1110 sq ft. based on 275-ton heats, 4.04 sq ft of hearth area per ton of ingots.

The overall thickness of the bottom at the center of the furnace is 39½ in., detailed as follows: Insulating concrete, 1 in.; burned chrome brick (two row lock courses, one soldier course) 18 in.; magnesite brick, 9 in.; rammed material, 11½ in.

Approximately 13 ft of each end of the hearth has 2 in. of insulating brick in addition to 2½ in. of first quality fireclay brick.

H. A. PARKER is Division Superintendent, Steel Producing, Fairless works, U. S. Steel Corp. This paper was presented before the AIME National Open Hearth Steel Committee, Buffalo, Apr. 22, 1953.

Front Wall and Back Wall

Below foreplate level the front wall is composed of 13½ in. of burned chrome brick, 9 in. of magnesite brick, and about 10 in. of rammed refractory. The back wall has a minimum thickness of 23½ in. of magnesite topped by about 10 in. of rammed material. The taphole is 6 in. diam.

Above foreplate level the front piers are encased magnesite chrome brick, 22½ in. thick for a height of 2 ft 6 in. The remaining top section of the piers are of metal encased magnesite chrome brick, 18 in. thick. The back wall above foreplate level is made up of magnesite-chrome brick 22½ in. thick covered by a tapering thickness of rammed material.

Furnace Roof

The main roof of the furnace has a span of 23 ft 10½ in. and a rise of 3 ft 6 in. The roof is 18 in. thick with every fourth ring a 24-in. rib. Super duty silica brick is used 4 ft up from the front skewback and 6 ft up from the back skewback, extending approximately from No. 1 door to No. 5 door inclusive. Balance of the roof is standard silica brick.

The port roof has a span of 20 ft 1½ in. and a rise of 2 ft 11¼ in. The roof is 18 in. thick with every sixth ring a 24-in. rib. The entire port roof is of silica brick.

The port end and side walls are generally 22½ in. thick, the outer wall of silica brick and the inner wall alternately 9 in. and 13½ in. magnesite chrome brick. A ¼-in. tie plate is placed between every fifth course of the basic brick. The two types of brick are banded at every course.

Structure and Binding

The port ends as well as the hearth section of the furnaces have slab buckstays. The front and back buckstays are 6 in. x 1 ft 6 in. The 12 front buckstays are water cooled. The back buckstays are offset at 51° to form the sloping backwall feature. The port and buckstays are 5 in. x 1 ft 3 in. The hearth buckstays are separated by the usual complement

of hearth castings and are rigidly bound at the top by heavy structural members. Skewbacks are 33 in. Carnegie Beams at 240 lb. The flanges were removed as required along the front. Bottom flanges of both front and back skewbacks are water cooled.

Furnace Below Charging Floor Level

Uptakes. The furnaces have two 61.15-sq ft area uptakes at each end. The uptake walls are magnesite chrome brick, 13½ in. thick. Suspended construction was utilized to replace many of the arches and brick structures below the uptakes. The chill walls and noses are suspended magnesite chrome brick and the fantails are suspended high alumina brick.

Slag Pockets. The furnaces have one slag pocket at each end, and they are constructed of 22½-in. first quality firebrick with a silica brick false wall of varying thickness. They are insulated with 4½ in. of insulating block. The floor is of silica sand. Each slag pocket has a cross-sectional area of 270.2 sq ft and an effective volume of 4250 cu ft. It is estimated that it will require 700 heats to fill the slag pockets to a height of 10 ft 6 in.

Regenerators. The furnaces are designed with multiple pass checkers. The regenerator roofs are of suspended semi-silica brick construction, 10 in. thick. This roof, as well as the fantail section, is insulated with 2 in. of block insulation. The regenerator walls are of first quality firebrick, generally 18 in. thick, and covered with 4½ in. of block insulation.

The first pass checkers are the solid flue type with 9x9 in. vertical openings which were constructed with interlocking bricks. Each first pass chamber has an effective volume of 3942 cu ft of checkerwork, or 7884 cu ft per furnace end. The dummy pass has a free area of 83.4 sq ft and is separated from the first and second chambers by 13½-in. thick first quality firebrick walls.

The second pass checkers are the solid flue type with 7½x7½-in. vertical flue openings. These checkers were constructed with one piece brick shaped to the flue dimension. Each second pass chamber has an effective volume of 3058 cu ft of checkerwork, or 6116 cu ft per furnace end. Thus, each furnace end has a total checkerwork volume of 14,000 cu ft, or slightly more than 50 cu ft per ton of steel.

Structural and Binding. The slag pocket and regenerator buckstays are all heavy I-beam sections and are encircled by two 14-in. WF beams at 426 lb. A third beam of this size encircles the furnace just below charging floor level.

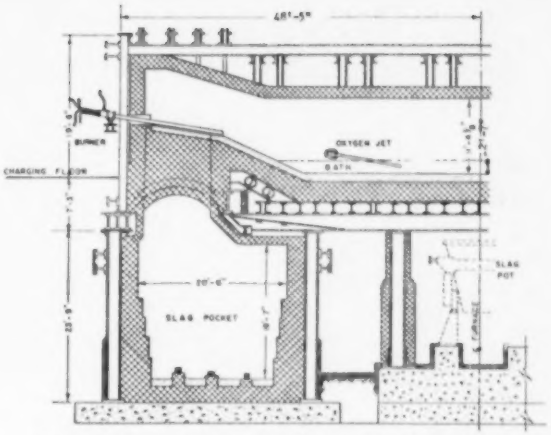

Fig. 2—Diagram shows longitudinal section through centerline of the new open hearth furnace. Two oxygen jet devices for decarburization are permanently mounted in the furnace backwall and can be swung out of the way when not in use.

Flues. There are separate flues from each regenerator chamber. They extend about 40 ft before combining into a common flue for each side of the furnace. At reversing valve location, each flue has a typical cross-sectional area of 42.6 sq ft, or 85.2 sq ft per furnace end. The common flues join into a single passage before dividing into the similar stack and waste heat boiler flues. At stack and waste heat boiler damper locations, each flue has a typical cross-sectional area of 53 sq ft.

Typically, the flue walls are second quality firebrick 13½ in. thick. They are backed with 4½ in. of insulating brick. The flue arches are semicircular and made of 9 in. second quality firebrick. They are covered with 4½ in. of insulating brick and 4½ in. of common brick. The flue floors are of second quality firebrick, 9 in. thick and laid on top of 2¼ in. of insulating concrete. Below the concrete are two 2¼ in. courses of common brick laid to form a drain floor. The regenerator floors also conform to this design. It should be mentioned that the top of flue floor is at elevation + 9 ft 4¾ in. and top kitchen floor is at elevation + 25 ft.

Stacks. The 225-ft high furnace stacks are the self-supporting type. They are of welded steel construction, fabricated from plate of varying thicknesses. The stack linings are second quality firebrick in thicknesses varying from 4½ in. at the top to 39 in. at the bottom. The stacks have bottom

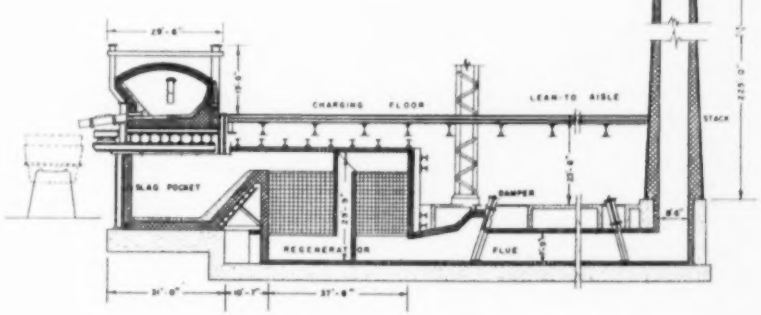

Fig. 3 — Cross-sectional view shows furnace details. Furnaces are designed with multiple pass checkers. Each furnace has a total checkerwork volume of 14,000 cu ft, or slightly more than 50 cu ft per ton of steel.

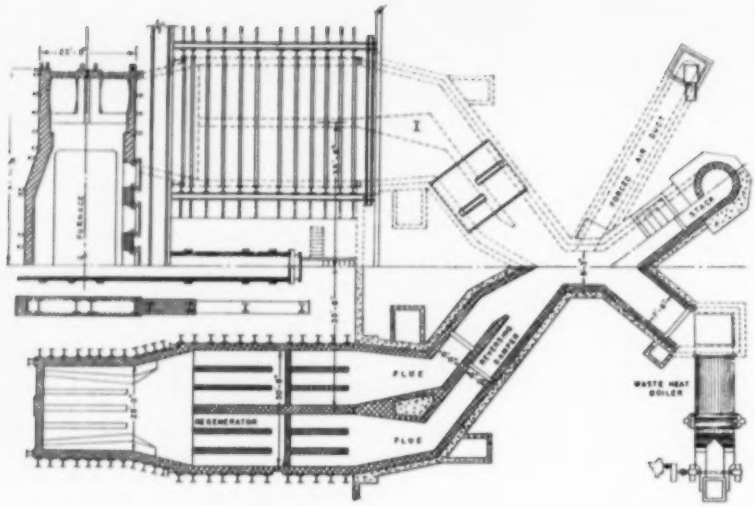

Fig. 4—Plan view of flue arrangement shows the separate flues from each regenerator chamber. The separate flues extend 40 ft before combining into a common flue for each side of the furnace. The common flues join into a single passage before dividing into the similar stack and waste heat boiler flues.

diameters of 8 ft 6 in. and top diameters of 9 ft 3 in. inside of brickwork.

Combustion System

Forced Draft Fans and Ducts. The forced draft fans are located in the open hearth kitchen. Each fan has a capacity to deliver 120,000 lb of air per hr (26,000 cfm) at a temperature of 70°F against a total static pressure of 6 in. water column. One feature of the Fairless open hearths heretofore not duplicated in many shops is the underfloor forced draft ductwork. The duct goes underground from the fan discharge and branches to each of the four reversing valves. By this arrangement, the reversing valves are located at a lower elevation, and thus provide additional room at kitchen floor level for blowing checkers, truck movements, furnace repair, etc. A bevel gear arrangement is employed for setting butterfly valves from the kitchen floor.

Fuel Burners. Fuel burners for the furnaces are the artillery water cooled type suitable for burning Bunker C fuel oil and/or coke oven tar. They are designed for a maximum fuel capacity of 1000 gal per hr of either oil or tar at pressure of 130 to 200 psig. Provision has also been made in the burner for piping oxygen for flame enrichment. There is no provision for gaseous fuel.

Waste Heat Boilers

Each furnace is provided with a horizontal tube type waste heat boiler containing 927 2½-in. tubes. The boilers have superheaters designed to raise the steam temperature to 620°F when the boiler is receiving 160,000 lb per hr of waste gas at 1150°F at entrance to the superheater. The boiler is designed for low draft loss and low exit temperature. Under the above conditions, the estimated waste gas temperature from the boiler will not exceed 550°F, and the steam pressure will not exceed 330 psig at the superheater outlet. Estimated production is 21,000 lb of steam per hr. A complete complement of instruments is provided for the waste heat boilers.

Induced Draft Fans

The induced draft fans have a maximum capacity of 235,000 lb of waste gas per hr at inlet conditions of 575°F and 29.92 in Hg abs and a static head of 8 in. water. The fans are driven by 250 hp DeLaval steam turbines, operating at 3920 rpm. The turbines are designed for maximum steam condition of 600 psig and 750°F, and have 10-in. exhausts and 4-in. steam inlets. The turbines exhaust to the low pressure steam system, 7½ psig.

Controls and Instruments

The open hearth is equipped with a complete set of automatic controls and instruments. They are located in a control house on the open hearth floor between the charging aisle and lean-to aisle. The panel board forms the front wall of the control house, and the instruments, control equipment, gages, meters, etc., are housed within the building. In general, the control system is the pneumatic type.

Furnace controls are designed for reversal by temperature difference, time interval, or manual operation. In addition to the air reversal valve, oil, tar, oxygen, and steam reversal valves are also provided.

A detailed description of controls and instruments and their functions would be a report in itself. Only those provided are listed. They are; automatic furnace reversal control, furnace pressure control, roof temperature control, fuel oil and fuel tar controls, total Btu control, checker differential temperature control, checker temperature recorder, flue temperature indicator, bath temperature recorder, steam flow control, oxygn flow control for combustion and decarburization, oil loop pressure control, tar loop pressure control, and viscosity control for oil and tar.

Oxygen Jet Devices

Each furnace is equipped with two oxygen jet devices for decarburization. They are permanently mounted at a location in the furnace backwall. The oxygen jets are designed to project from the furnace backwall when being used, and to swing to a position parallel to the back of the furnace when not in use. They operate on a track arrangement making their position in the furnace adjustable. The jets are water cooled.

Production

Actual evaluation of furnace production cannot be made now because of the short time the furnaces have been in operation.

British Producing Germanium From Flue Dust

BRITISH success in extracting significant quantities of germanium from gas works' flue dusts has been one of the prime forces in promoting similar research in the United States. Pittsburgh Consolidation Coal Co. and Pennsylvania Coal & Coke Co. are two of the larger U. S. firms with germanium from flue dust research programs.

British interest in germanium started in 1933 when V. M. Goldschmidt reported that some coals from the Yard Seam of Northumberland and Durham contained 30 to 50 ppm of germanium.

However, in a recent survey of all the United Kingdom's major coalfields by the Fuel Research Station of the Dept. of Scientific and Industrial Research, it was found that Goldschmidt's estimate was rather high. Ten samples of coal taken from the seam he investigated showed germanium content of 2 to 22 ppm with an average content of about 7 ppm. It appears that germanium occurs in all the major coalfields and is not localized in a few seams.

The germanium may be associated with carbonaceous material in the coal rather than with another mineral. It is believed that this is partly the reason that germanium is likely to be found in the flues of producer plants rather than in flues from ovens where coal is initially carbonized. Dry coal ash produced from dirty coals have shown an average germanium content of 0.006 pct, while clean coal ash averaged about 0.013 pct.

About 12 times the amount of germanium will be found in flue dust in comparison to ash. The amount of germanium produced from dirty and clean coals should be 0.072 pct and 0.156 pct respectively on the average. The difference between flue dust and ash may be even greater because deposits of flue dusts have been found to contain up to 2 pct germanium.

Generally, it has been found that germanium content of dust in the CO_2 flue and in the waste heat boiler area is greater than germanium content of dust from the CO flue. However, flue dust at the South Metropolitan Gas Co. plant was found to have a higher germanium content than that from around the waste heat boiler. Majority of Britain's large gas works have been surveyed for germanium bearing flue dust and are contributing their outputs to the nation's supply of germanium metal.

Johnson Mathey & Co. Ltd. considered a number of processes before deciding to investigate a metallurgical method. The firm hopes to attain an output of about 350 kg annually using flue dust from producer plants as raw material.

The initial step in germanium extraction from flue dust is smelting the dust with known collectors. Iron, nickel, and copper are suitable collectors for germanium, while copper is used for gallium collection. Flue dust is smelted with soda and lime as fluxes for the silica and alumina and with copper oxide and carbon to provide copper for the collection of the germanium and gallium. The copper-iron regulus obtained contains more than 90 pct of the germanium and 80 pct of the gallium.

Dusts high in sulphate were given a preliminary roasting to reduce sulphur content to 5 pct. This avoided the excessive formation of matte, which by taking up the copper, reduced the amount of gallium extracted into the regulus. The regulus contains about 3 to 4 pct germanium, and usually 90 to 95 pct of the available germanium is extracted. Most of the lost germanium is deposited in the flue of the furnace being used. The flue is regularly cleaned and the dust returned for processing.

To recover rare elements from the regulus, it is first converted into a solution of trichlorides. All the germanium, with some of the arsenic is recovered from the solution by distillation. Most economical method is to treat the regulus with a current of chlorine under a dilute solution of ferric chloride, which acts as a catalyst. Because the process is highly exothermic and could be applied cold without use of external heat, the rate of reaction is controlled by the rate chlorine is added to the system.

The resulting chloride solution was siphoned or blown into a battery of Pyrex stills heated by electric mantles. Vapors pass through standard Pyrex containers and the condensates flowed through a common pipeline to a Pyrex receiver. This was also connected through an empty carboy serving as a trap to a water-filled carboy collecting and hydrolizing noncondensed vapors of arsenic and germanium chlorides.

Distillation is started by slowly dropping sufficient concentrated sulphuric acid into the boiling solution to liberate enough hydrochloric acid to render the solution in the still about 7N with respect to the acid. Distillation is continued until about 25 pct of the still content is evaporated. Under these conditions the acidity of the condensate is such that it is separated into two layers. The lower layer consists of germanium tetrachloride containing up to 20 pct of arsenic trichloride and the upper layer consists of constantly boiling hydrochloric acid containing arsenic trichloride almost free of germanium.

The crude germanium tetrachloride, with a boiling point of 84°C, is separated from arsenic trichloride by careful fractional distillation. Prolonged refluxing of the liquid through a column packed with clean copper turnings is the most satisfactory way of eliminating the residual arsenic.

After refluxing for 12 to 15 hr, pure germanium containing less than 1 part arsenic in 10^7 germanium was obtained. The chloride was hydrolized to dioxide and washed free from hydrochloric acid and dried at 150°C. To produce germanium metal the oxide is placed in a pure graphite boat and heated in a tube furnace in hydrogen to about 650°C. At 650°C the hydrogen is replaced with pure nitrogen and temperature raised to 1000°C to melt the previously formed powder into an ingot. An ingot molded in a hydrogen atmosphere becomes porous on cooling because molten germanium absorbs hydrogen liberated during solidification, producing minute blowholes.

This is an abstract of an article on Production and Uses of Germanium by J. A. Gay, that appeared in the June 1953 issue of *Chemical & Process Engineering*, published by Leonard Hill Ltd., London.

Ion Exchange Finds Wider Use In Concentration And Recovery of Metals from Dilute Solutions

by A. B. Mindler and C. F. Paulson

TREMENDOUS increased demand in the near future for metals recently considered rare and unimportant, and the strategic position of these metals in rapidly developing new industries is vividly pointed up in the Paley Report.[1] It emphasizes the increasing consumption of ferrous and nonferrous metals and the dire need for technological improvements in the manufacture of metals from lower grade, complex ores. It implies the necessity for wiser use of our metal supply and the recovery of metals now needlessly going to waste. Ion exchange, a newly recognized unit operation, has been found useful in a number of industries for realizing some of these objectives and this unique phenomenon is destined to be more widely employed.

Ion exchange has been taking place since creation of the earth. Our soils, formed from erosion, oxidation and hydration, possess both cation and anion exchange properties and many minerals have substantial ion exchange capacity.[2] In fact, the common name—zeolites—used for water softening ion exchangers is borrowed from the geologists' nomenclature. One of the earliest commercial ion exchangers was a processed naturally occurring glauconite, a hydrous aluminum silicate. This ion exchanger is still in use in many water softening installations. However, metallurgical and chemical engineers are interested primarily in the organic ion exchangers because of their superior chemical properties. The first of these was a sulfonated coal marketed in 1935. Synthetic resin ion exchangers were discovered by Adams and Holmes in England about the same time. The early ion exchange resins have been greatly improved in both physical structure and chemical characteristics. A classification of the most important commercially available ion exchanger is shown in Table I.

Physical and Chemical Characteristics

Ion exchange is the reversible interchange of ions between a solid and a liquid in which there is no substantial change in structure of the solid. Commercially available ion exchangers are granular or spherical solids with a size approximately 90 pct through 16 on 50 mesh (U. S. Standard Sieves) ranging in color from white through brown to black. They are hard, insoluble particles of organic structure with active chemical groups bound to a crosslinked matrix. The active groups are sulfonic groups in most cation exchangers although cation exchangers with carboxylic or phosphonic groups are also available. In anion exchangers the active groups are amino groups in weakly basic resins, quaternary ammonium groups in strong base resins and mixtures of these in resins of intermediate strength. Numerous papers[2,4,5,6] and several books[7,8,9] have been published discussing ion exchange equilibria and kinetics.

Titration curves of cation exchangers indicate capacities for exchange at various pH levels for both cation and anion exchangers. These are shown in Fig. 1. Unfortunately these curves cannot be used for accurately evaluating ion exchangers for commercial work because other considerations such as the Law of Mass Action, Donnan Equilibrium considerations and several other known and unknown phenomena influence the performance of ion exchangers. These phenomena influence the economics of ion exchange by limiting the operating capacity below the equilibrium or total capacity. In general, ions of greater atomic weight (or smaller hydrated ionic size) are held in preference to those of low atomic weight. Polyvalent ions are held in preference to monovalent ions.

Acid regenerated cation exchangers concentrate metal cations in solutions where they are present as dilute solutions of salts. This may be done even in the presence of surprisingly high concentrations of strong acids. The capacity of a sulfonated crosslinked styrene copolymer cation exchange resin is of the order of 2 to 2.5 lb of copper per cu ft of resin. The conventional ratings for ion exchangers are the operating capacities expressed as kgr of calcium carbonate per cu ft; 1 kgr per cu ft equals 0.00286 lb equivalents per cu ft. Operating capacities are only a portion of the ultimate or saturated capacities for adsorbing ions. If a mixture of cations is passed through a cation exchanger bed, all metal cations will be adsorbed until breakthrough occurs. Thereafter, the ions held preferentially are those with higher valence and higher atomic number, the ions of lower valence being displaced from the bed.

Anion exchangers may be used to neutralize acids or to exchange anions. In general, weakly basic resins are used to adsorb strong acids and these are usually regenerated with soda ash. Strong base resins are used to remove weakly dissociated acids and caustic soda is used for regeneration.

Anion exchangers may be used for exchanging anions other than hydroxyl and in these applications salts, acids or mixtures of salts and acids may be used for regeneration.

Equipment

Practically all ion exchange equipment used now is of the pressure percolation type similar to pressure sand filters. A cutaway view of a typical water demineralizing plant is shown in Fig. 2. The size of commercial ion exchange equipment for applications

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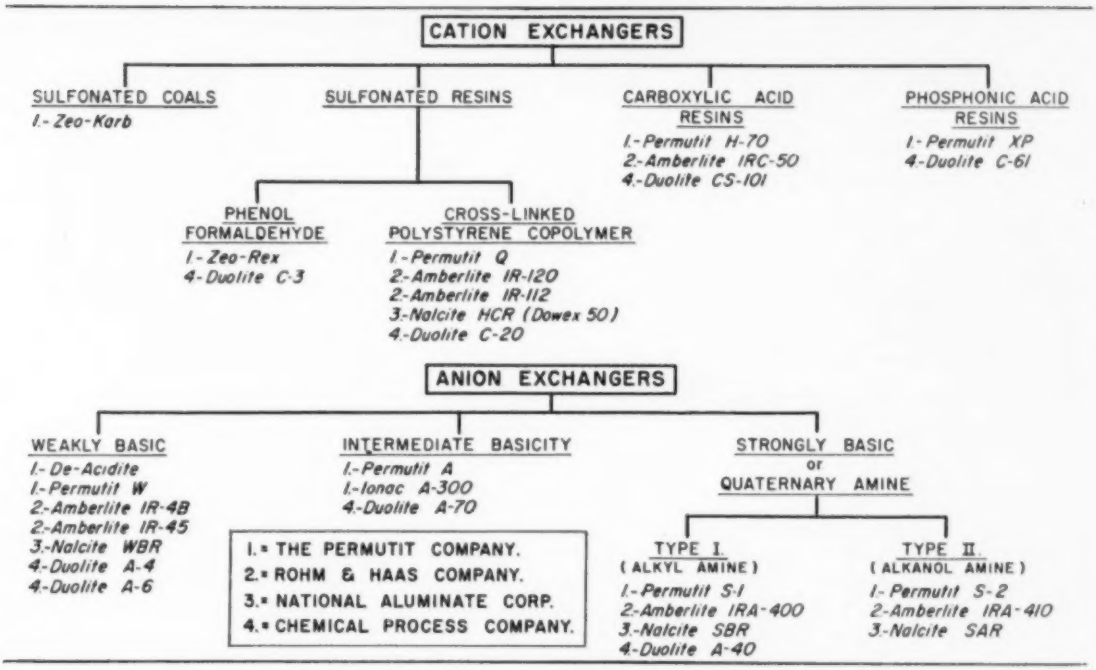
Table I. Commercially Available Ion Exchangers



in the water conditioning and other fields may range from several inches diameter to 12 or 14 ft diam. The larger units may be 12 ft or more in the straight of the shell. Equipment size depends on the capacity required and on the flow rate. Gravity flow ion exchange units have been built, some up to 24 ft diam, but this type of equipment is more difficult to control and generally is as expensive as the pressure type.

Design characteristics of the distributor systems and collector system or underdrain are extremely important to obtain proper hydraulic distribution. The ion exchanger bed usually is supported on a graded gravel bed. Obviously, the equipment must be designed for suitable resistance to corrosion by the solutions to be treated. The ion exchanger bed may be 24 in. deep minimum, to 6 or 8 ft maximum, although slightly shallower and deeper beds have been successful. Adequate rising space must be provided for proper backwashing to loosen and regrade the bed and to cleanse it of suspended substances filtered out during the run. Rising space generally is 75 pct for cation exchange resins and 100 pct for anion exchange resins, based on bed depth.

Ion exchange equipment may be designed for manual, completely automatic, or semiautomatic pushbutton operation. Automatic control frequently is desirable, particularly in complex processes because it saves labor and chemicals, assures uniform results, and is reliable.[10]

Equipment for laboratory test and development work generally employs glass tube columns for percolation operation and is inexpensive to set up and simple to operate.[11]

Uses of Ion Exchange

Two main uses of ion exchange in the past in the metals field have been concentration of metals in dilute solution and separation of the components of mixtures of ions. Most of the experimental work and practically all of the commercial installations pertain to the concentration of metals. Future emphasis will be placed in this field. The reason is that ion exchange is peculiarly adapted to concentrating constituents present in dilute solutions, and the more dilute—the greater is the economic advantage when compared with conventional processes such as chemical precipitation, electrolysis or evaporation. In the separation of components in mixtures, it must be admitted that today's ion exchangers are not completely selective in the adsorption portion of the cycle, and separation during desorption or elution requires special techniques. Examples of the most important ion exchange processes developed in the past in the field of hydrometallurgy include most types of cation and anion exchange.

Concentration and Recovery

Cation exchange (sodium cycle)—The sodium cycle hasn't often been used in metallurgical applications because of interference of the sodium ion in subsequent recovery of the metal from the regenerant effluent. However, at least one plant recovers zinc from a viscose rayon plant acid waste in which a mixed salt-acid regenerant is employed thus operating partially in the sodium cycle. The waste contains approximately 300 ppm zinc sulfate in an acid solution containing 600 ppm H_2SO_4 and 2700 ppm sodium sulfate. The zinc is regenerated off the sulfonated crosslinked polystyrene copolymer, Permutit Q, at about 6 to 8 pct zinc sulfate.

Cation exchange (hydrogen cycle)—Because ion exchange merely concentrates dilute solutions of metals to about 10 pct salt solutions, the metals must be recovered from these solutions either directly or by feeding them to a part of the process where they will join other process streams for precipitation. The most frequently used process is electrolysis, which is generally conducted from acid solutions. It follows

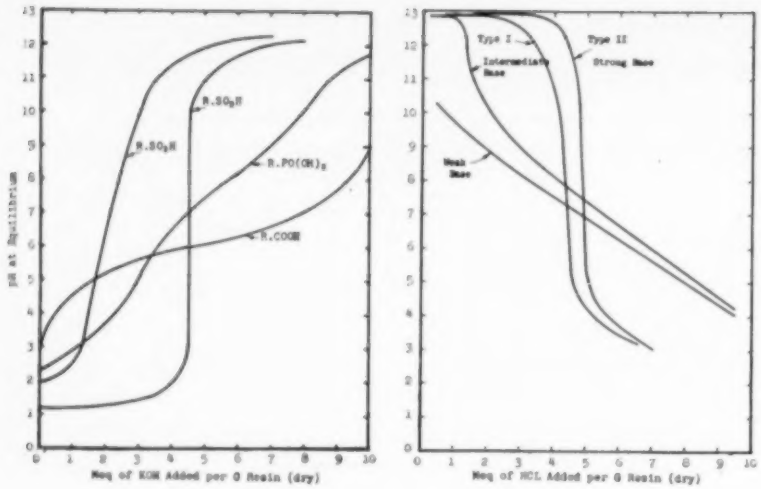


Fig. 1—Titration curves of hydrogen cation exchangers in 1.0N potassium chloride, left, and titration curves of anion exchangers on 1.0N potassium chloride, right, indicate capacities for exchange at various pH levels. Various phenomena, however, prevent use of these curves for evaluating ion exchangers for commercial work.

naturally that the acid or hydrogen cycle of the ion exchangers is the most adaptable process, at least for acid leach process. However, even in other applications the hydrogen cycle is generally used because of the effectiveness of acid elution or regeneration. One of the earliest installations for metal recovery was a plant installed in Germany for recovering copper and ammonium ions from cuprammonium rayon wastes.[12] Copper recovery from rayon waste is also practiced in this country on a large scale and concentrations of the order of 2000 fold realized.

Another process in which a cation exchanger is used for metal recovery is still in the development stage. Some tin plating operations are conducted from alkaline baths and the rinse waters contain considerable quantities of sodium stannate. By passing this solution upflow through a hydrogen cation exchanger the sodium stannate is converted to insoluble stannic acid. This floc may be concentrated by settling and then converted to stannous oxide by heat. It is interesting to note that the rinse water may be recovered, together with its heat value, for reuse.[13]

Anion exchange (hydroxyl cycle)—Anion exchangers may be used for concentration of metal complex present as anions and a number of installations have been made to recover chromate from anodizing and chrome plating rinses. The anion exchanger, after exhaustion to its capacity for adsorbing chromate, is regenerated with sodium hydroxide to form sodium chromate. The regenerant effluent is then passed through a hydrogen exchanger where the sodium chromate is converted to chromic acid and the excess sodium hydroxide is converted to water. The chromic acid solution is concentrated and returned to the bath or directly to the save rinse tank. Highly basic anion exchangers are employed in this process.[14]

Anion exchange (salt cycle)—One of the earliest publications in the field of metal recovery by ion exchange described the recovery of metal anion complexes by exchanging them for chloride or sulfate anions on weakly basic anion exchange resins. Experimental data was presented on the adsorption of chromate, molybdate, ferrocyanide, vanadate anions and precious metal complexes. Such processes may be useful for concentrating certain metals as salts then converting them to insoluble acids and further processing to recover metal oxides.[15]

An interesting variation of this type of process can be accomplished with these metals which form stable anionic complexes in highly acid solution. For instance, iron in strong hydrochloric acid forms the anion $[FeCl_4]^-$. This anion can be adsorbed very completely from acid solution by a highly basic anion exchanger. It can then be removed by passing water through the anion exchanger displacing the acid, rendering the complex unstable, and allowing it to be rinsed out as $FeCl_3$. Using this technique, metals forming such complexes can be separated from those which do not, although highly acid solutions are required.[16]

Anion exchange (resin in pulp)—During the last 10 years a new process, the Krebs Process,[17] has come into use in the gold mining industry, namely the recovery of gold from slimy, difficultly clarified ores by adsorption of the gold on granular activated materials. Similar to this process is one which has been under development involving ion exchange resins for adsorbing gold from cyanide pulp. The gold cyanide anion complex is adsorbed on an anion exchanger and is removed by caustic.[18,19] The regeneration is followed by zinc dust precipitation in contrast to electrowinning in the Krebs Process. This process is promising for treatment of slimy ores.

Separation by Ion Exchange

Cation Exchange—One of the most interesting and extensive pieces of ion exchange work in recent years was the separation of rare earths under U. S. Atomic Energy Commission auspices at Iowa State College and Oak Ridge National Laboratory.[20] This work resulted in the expeditious separation of the rare earths for the first time in macro quantities and led to the identification of element 61, promethium.[21] The mixture of metal cations was adsorbed from the salt solution on a hydrogen exchange resin, but only to a fraction of the bed capacity. The layer of mixed cations was then displaced or eluted down the ion exchange column by complexing the metals. Among the complexing agents were solutions of ammonium citrate and citric acid as various pH's. The eluted metals appeared in the effluent in sharp bands.

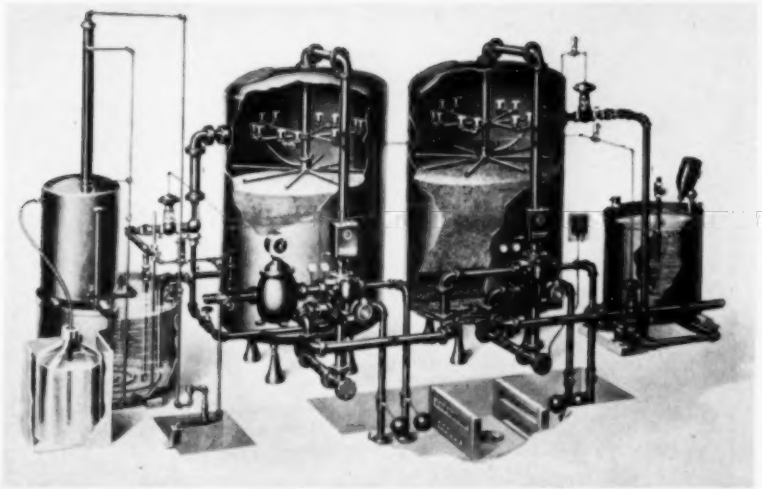


Fig. 2—A typical water demineralizing plant is shown in cutaway view. Almost all ion exchange equipment used today is of the pressure percolation type similar to pressure sand filters. Equipment may be designed for manual, completely automatic, or semi-automatic operation.

Anion Exchange—Highly basic anion exchangers have recently been used at Teddington Laboratory, England, in cooperation with the Rand School of Mines, South Africa, for the separation of metals in a complex Canadian gold ore. The mixture of copper, zinc, nickel, iron, gold and silver was adsorbed as the cyanides on the anion exchanger. Copper and zinc were eluted by treatment with caustic; iron and nickel by treatment with hydrochloric acid; and gold and silver by treatment with acidified acetone.[22]

Limitations

Since ion exchange reactions are controlled largely by the Law of Mass Action and exchange proceeds rigidly in chemical equivalents there must be certain limitations in the application of ion exchange. An ion exchanger is effective for adsorbing a specific ion only if the concentration of interfering ions in the solution is below that of the ion to be adsorbed. Thus, while it is possible to adsorb iron ions from a phosphoric acid pickling solution of 35 pct, the removal of iron from a 5 pct sulfuric acid is not feasible. This is due to the difference in concentration and activity of the interfering hydrogen ion. Likewise, separation of mixtures of ions depends on the relative concentrations and characteristics of the ions comprising the mixture. Difficult separations of rare earths have been developed, but these depend on special elution procedures, not on differences in adsorption. Since each ion exchanger has a limited capacity for adsorption of ions, the concentration of the regenerant or elution effluent is limited. Even by employing recycling procedures for regenerant effluents, the void space between ion exchange particles, the imbibed solution inside the particles, and resistance to diffusion of ions by the liquid film and the resin structure all contribute to a limited concentration of salts in the elution solutions.

There are also certain limitations in the chemical and physical characteristics of ion exchanger materials. Recently developed ion exchange resins possess remarkable stability toward reducing conditions, highly oxidizing conditions, extreme alkaline or acidic pH, and high temperatures over many cycles. The styrene copolymer cation exchanger, Permutit Q, for example, is unharmed in over a thousand cycles of treating solutions containing 1000 ppm chlorine, or at pH 11 to 12 or in softening hot process water at 250°F. Attrition rates under normal conditions of operation are only a few percent per year. However, certain solutions contain substances which may be adsorbed by the ion exchanger and not completely regenerated off by the conventional regeneration or elution procedures. Such difficulties result in gradually decreased capacities which can usually be restored by appropriate chemical treatment applied at intervals. Lead and barium, for example, are difficult to remove from sulfonated cation exchangers. Hydrochloric acid treatments or other special chemical treatments may be required intermittently where such ions may be present. Certain complex metal anions may also act as poisons and require removal by chemical treatment at intervals.

Physical poisoning of the ion exchanger may also occur. In conventional ion exchange equipment of the percolation type the solutions to be treated must be clear and free of suspended matter. Generally turbidities above 10 or 20 ppm lead to difficulties unless the periods are short between backwashes. Precipitation in the bed during the adsorption period or during the regeneration or elution portion of the cycle also may lead to rapid decreases in capacity and efficiency.

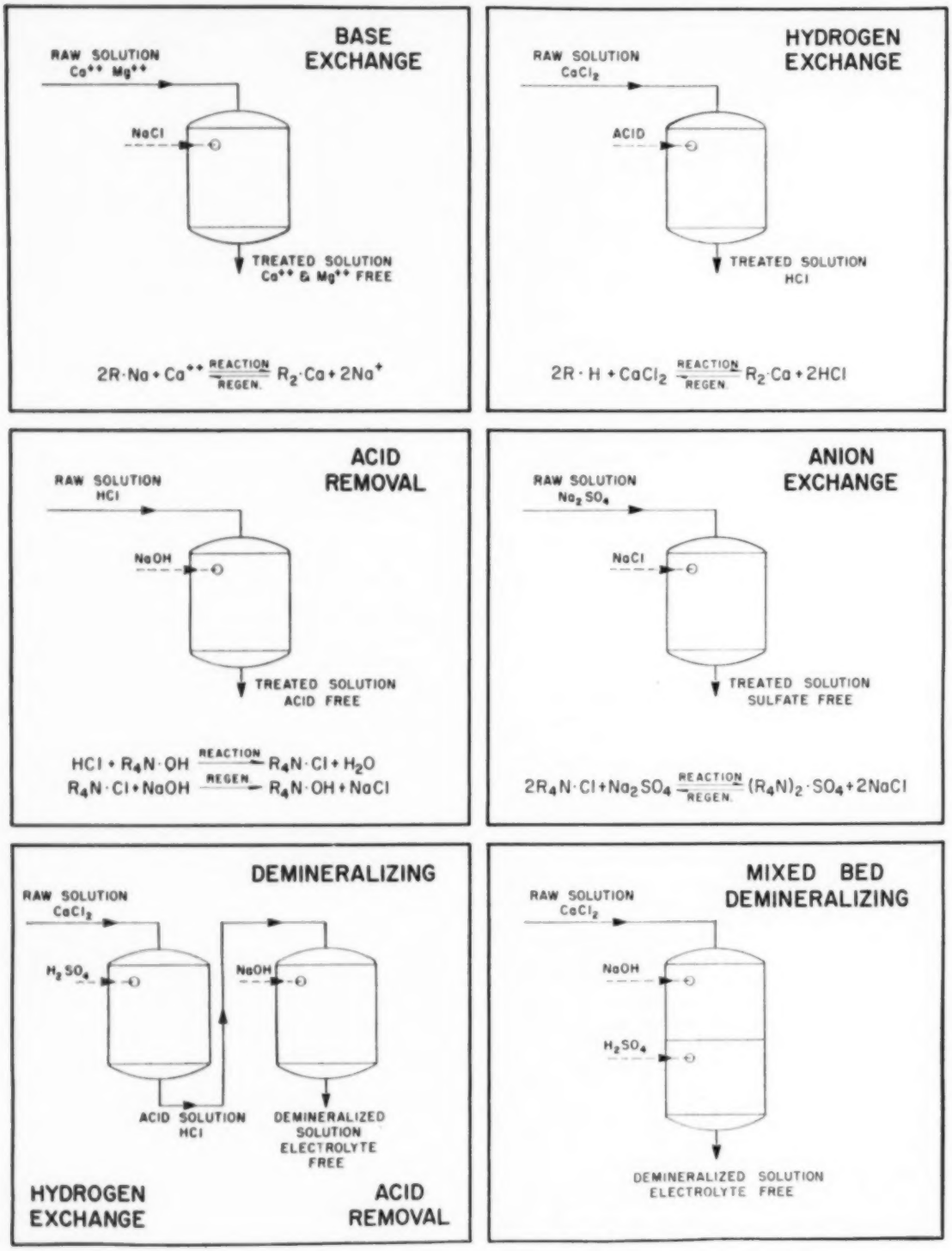
Possible Applications in Hydrometallurgy

The foregoing discussion of ion exchange immediately suggests several applications in the mining and metallurgical industry. Among these are:

1—Concentration of metal values from
  A—Mine waters
  B—Heap leaching, leaching in place or dilute countercurrent decantation washings
2—Separation of mixtures of metals as salts
3—Purification of electrolyte
4—Conversion of salt to acid or base
5—Regeneration of leach solutions
6—Resin in pulp

Concentration—Ion exchange can take metals from dilute solutions such as occur in mine waters, heap leaching, leaching in place or countercurrent decantation system and return these as about 10 pct solutions of the metal salt at low operating costs. Most of the excess acid employed for eluting the adsorbed metal will be found in electrolyte solution.

Flow Sheets of Various Ion Exchange Processes



By proper flow sheet design it should be possible to reduce the number of thickeners used for washing by employing ion exchange to concentrate dilute values. In countercurrent decantation procedures an ion exchange installation may be economical for concentrating dilute washes thus decreasing the dissolved losses to tailings without penalizing the water balance. In those operations where filters are employed, the production of low value tailings often necessitates extensive washing of the cake. In order

to maintain the solution balance, evaporators are sometimes employed. Ion exchange should be a more economical means of concentrating such dilute solutions and in contrast to evaporation the more dilute the values the more favorable does ion exchange become. The regenerant effluent or elution solution from the ion exchanger may be added directly to the solutions going to the precipitation room or to leach or to earlier washing stages.

When electricity is cheap and scrap iron expensive, ion exchange combined with electrolysis of the regenerant or elution solution may be more economical than cementation. The ion exchanger would be used for concentrating the leach solution to the point where electrolysis can be economically applied.

Separation—Ion exchangers may be useful for separating mixtures of metal salts into the several components but such processes are most likely to be economical only for those metals of relatively high unit value. Fortunately, other more economical processes are effective for the separation of metals of low unit value. Separation of metals in solution by ion exchange, except for metals which can stand the high cost involved in available procedures, must await the development of more selective ion exchangers and better techniques. Such techniques include the use of continuous countercurrent adsorption and elution.

Purification—Relatively little work has been conducted on the purification of process or electrolyte solutions by ion exchange in hydrometallurgy. However, since ions are adsorbed preferentially, the higher the valence and the higher the atomic number, purification of process solutions should be possible. The concentration of ferric iron, for example, should be reduced substantially in the presence of divalent ions such as copper from leaches. The regenerant effluent will contain the ferric iron as sulfate together with the divalent metal sulfates and excess acid. This should be useful for reuse in leaching, in the case of some copper operations.

Metathesis—It is easy to convert salts to acids by ion exchange. For example, it may be desired to convert a sodium salt of a metal anion complex to the corresponding acid or to another salt of the anion, say the ammonium salt. This is done by using cation exchange in the appropriate cycle or by converting to the acid, then neutralizing. Alternatively, the metal may be present in cation form as the sulfate but desired as the chloride. This conversion is accomplished by use of the anion exchanger chloride, exchanging chloride from the resin for sulfate in solution.

Resin in Pulp—Perhaps one of the most promising fields in hydrometallurgy for employing the unique properties of ion exchangers lies in their application to removing metal values from pulps. CCD systems and filtration equipment, especially of corrosion resistant design, comprise a large portion of the investment in hydrometallurgical plants. If the ion exchanger can be contacted directly with the pulp for adsorption of the metal value and then separated for elution of the metal from the ion exchanger, considerable savings in investment, labor, pumping and loss to tailings may be effected. Such operation will require fine grinding and sand-slimes separation. Thickening and washing operations can then be reduced considerably since residual metal values can be picked up by the ion exchanger without upsetting the solution balance.

Another interesting possibility of employing resin in pulp is the use of fluid energy grinding for effecting grinds to micron size which should be amenable to leaching very rapidly with low acid concentration. Leaching might be complete in a few minutes during pumping of the slurry or even simultaneously with adsorption of the metal value.

Equipment for applying ion exchange to pulps, slurries, and other materials containing large quantities of suspended solids on a continuous countercurrent basis is being developed.

The *Battelle Technical Review*, June 1953 mentions that—"An important new development is the use of ion-exchange resins in the process that is being applied for extracting uranium from gold ores at South Africa's gold mines. In this process, the uranium is leached from the ores by means of sulfuric acid wich can be made from pyrites found in the area. The resulting solution is then passed over ion-exchange resins to obtain the uranium." However, few additional details have been released for publication.[23, 24, 25]

The application of ion exchange to hydrometallurgy is destined to contribute immensely to the economy of our country in the future. It will make possible the economic solution of the many problems involved in working up the progressively poorer and more complex ores which must be worked in the immediate future. The unique properties of ion exchangers fill the gaps of the other unit operations which have been so well developed and so wisely employed in hydrometallurgy.

Bibliography

[1] Report of President's Materials Policy Commission —Outlook for Commodities, Vol. II, (1952)

[2] H. F. Walton: J. Franklin Inst. **232**, 305 (1941)

[3] G. E. Boyd, J. Schubert, and A. W. Adamson: JACS **69**, 2818, (1947)

[4] W. C. Bauman and J. Eickhorn: JACS **69**, 2830, (1947)

[5] H. P. Gregor: JACS **70**, 1293 (1948)

[6] R. Kunin and R. E. Barry: Ind. Engr. Chem. **41**, 1269 (1949)

[7] F. C. Nachod: Ion Exchange Academic Press (1949)

[8] R. Kunin and R. J. Myers: Ion Exchange Resins, John Wiley & Sons (1950)

[9] Olof Samuelson: Ion Exchangers in Analytical Chemistry, John Wiley & Sons (1953)

[10] C. M. Guldner: Conference on Instrumentation in Water, Sewage and Industrial Waste Treatment, Manhattan College, May 14, 1953. To Be Published—

[11] Permutit Co., Manual for Laboratory Use of Ion Exchangers (1952)

[12] N. E. Topp: Report PB 19585 OTS Washington, D. C. (1946)

[13] A. B. Mindler, M. E. Gilwood, and A. H. Saunders: Ind. Engr. Chem. **43**, 1079 (1951)

[14] C. F. Paulson: Plating **39**, 1330 (1952)

[15] S. Sussman, F. C. Nachod, and W. Wood: Ind. Eng. Chem. **37**, 618—(1945)

[16] K. A. Kraus and G. E. Moore: JACS **75**, 1460 (1953)

[17] R. W. Krebs: US 2,476,420 July 19, 1949

[18] F. C. Nachod: US 2,371,119 issued Mar. 6, 1945

[19] S. J. Hussey: R.I. 4374 U.S. Dept. of Interior, Washington, D. C. (1949)

[20] Symposium JACS **69**, 2769—(1949)

[21] J. A. Marinsky, L. E. Glendenin, and C. D. Coryell: JACS **69**, 2781—(1947)

[22] F. H. Burstall, P. F. Forest, N. F. Kember, and R. A. Wells: 122 Annual ACS Meeting, Atlantic City, N. J.

[23] G. A. Lutz: Battelle Technical Review, June (1953)

[24] Anon.: South African Mining and Engineering Journal, p. 243, 251 Oct. 18, 1952

[25] Chemical Engineering, **60**, No. 2, 198.

Deoxidation and Degasification Practice For Basic Electric Furnace Alloy Steels

by A. L. Ascik

DEOXIDATION is one of the most fascinating subjects in steelmaking. Frequently related to deoxidation are such technological properties as castability, hot workability, and internal and external defects detected at the early stage of steelmaking. Longitudinal and transverse physical properties, inclusions, hardenability, edge properties of tool steels, and other properties in finished products and in customers' factories are also related.

Despite years of experience on many grades of steel, and absorbtion of all the literature on deoxidation, the question "what actually is deoxidation and what does it mean?" causes hesitation before an answer is attempted. Yet, steelmaking constitutes a continuous struggle with oxygen regardless of its form in steel. One approach to definition of deoxidation is consideration of the opposite process, *oxidation*. It can be assumed that whatever oxygen does to iron, it does to steel. Fig. 1 presents the relationship between iron and oxygen. As temperature increases, solubility of oxygen, in the form of FeO, increases. The following conclusions are suggested to the operational man:

1—Oxidation changes with temperature. Steel can be oxidized or deoxidized without additions by lowering or raising temperature of the fluid metal.

2—A degree of oxidation/deoxidation can be measured, i.e., the quantity of oxygen dissolved in steel at a given temperature. This quantity frequently is called equilibrium or residual oxygen.

Introducing Si into the iron oxygen system considerably reduces the quantity of residual oxygen, as shown in the lower diagram of Fig. 2. However, the temperature factor remains decisive. Similar curves can be found for almost all elements of high affinity for oxygen.

Fig. 3 illustrates more recent results of Hilty's investigations on deoxidizing power of silicon, manganese, and aluminum and combinations of these elements at 1600°C. Completing the picture of deoxidizing abilities of regular elements contained in steel, Marshe's C curve and an old curve of Cr from *Basic Open Hearth Steelmaking* was plotted on the same diagram.

The curves show relative changes in quantities of residual oxygen in the presence of various deoxidizers. Their quantitative values cannot be transferred to operational conditions because the curves were based on laboratory figures and under specific atmospheric conditions. In commercial steelmaking action of slag and oxygen contained in the surrounding atmosphere indicates that figures concerning residual oxygen are considerably higher than those shown in the diagram. However, the diagrams serve to explain certain phenomena.

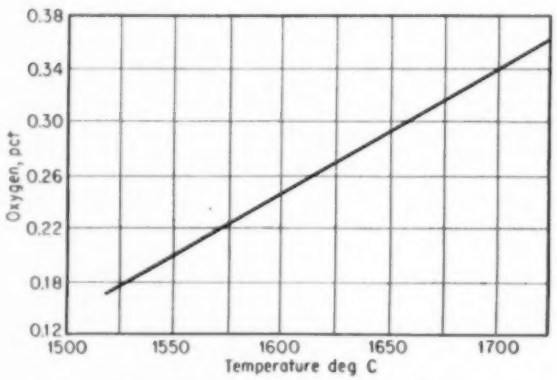


Fig. 1—This graph of the solubility of oxygen in pure iron shows the effect of temperature on oxygen solubility.

Importance of the effect of temperature on the degree of oxidation can be seen. The diagrams show why bath temperature must be accurately controlled. The diagrams indicate that to meet the same specified analysis for Si and Mn, their additions will vary with grades and manner in which the grades are made. For example, in making straight C steels of 0.15 pct C and 0.50 pct C, both with final 0.50 to 0.60 pct Mn and 0.20 to 0.30 pct Si, the diagrams show inherently high residual oxygen in 0.15 pct C grade. If in addition the bath temperatures vary from heat to heat, it requires an experienced steelmaker to calculate the losses of Si and Mn to meet the specified range of analysis. If temperature is controlled, additions can be determined in advance and if 10 pct can be cut on each Mn and Si addition, a saving of 60¢ per ton will be realized.

It can be seen at approximately 0.20 pct C, in the diagram, that carbon individually, is a stronger deoxidizer than Cr, Mn, Si, individually or in combination.

If the steelmaker keeps in mind that carbon and temperature factors are decisive in the entire procedure of deoxidation, the final steps such as addition of more powerful elements become routine. Stronger deoxidizers such as Al, Ti, and Zr usually are added shortly before tap or in the ladle because their deoxidizing action is temporary. If held in the fluid bath longer, they are completely oxidized and residual oxygen in the bath reaches the same figure

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as before the addition. It is believed that if the use of strong deoxidizers is beneficial it is not because the bath is deoxidized better, but because of creation of fine submicroscopic oxides of these elements dispersed in the mass of steel, or lattice, or grain boundaries, changing some technological features and properties of steel.

The continuous fight against oxygen in practical steelmaking seems to promote a trend toward deoxidizing the fluid bath completely. However, there are peculiar phenomena in steelmaking. It definitely is known that in practice heats must be worked out and tapped hot to get a high degree of cleanliness. Hot working and tapping of heats means high residual oxygen in the bath. This would indicate that the problem of inclusions has nothing to do with deoxidation, despite the fact that almost all inclusions found in steel are oxides. Contrarily, it has been found that a lower degree of cleanliness results when stronger deoxidizers are added or cold tapping is attempted to diminish residual oxygen in a hot fluid bath. Ordnance grades of steel, particularly those tested for macro and transverse physical properties, when tapped cold or more completely deoxidized, tend to show mediocre properties when compared with steels tapped with higher residual oxygen. Proper theoretical explanations for these phenomena is lacking. However, there is strong indication that good steelmaking does not only rely on deep deoxidation. Chemical processes and reactions by themselves are not responsible for good steel. No less a part is played by some methods which properly fall within the realm of the laws of physics. Up to this point, all that has been said deals with the fluid bath in the furnace. Steelmaking's second stage is metal pouring and solidification.

Steel is gradually cooled until solidification in castings or ingots. In accordance with previous statements, lowering temperature of the fluid steel means nothing less than deoxidation. No matter what the state of residual oxygen is in the furnace, the deoxidation process will continue to take place during all pouring and solidification periods until the last drop of metal is solidified. Visible examples of this self-deoxidation is in rimmed or semi-killed grades.

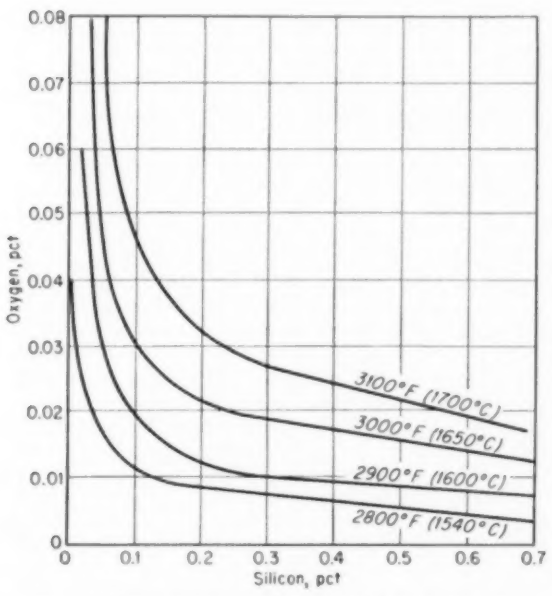

Fig. 2—These curves showing the deoxidizing power of silicon at various temperatures are typical of curves found for most elements of high affinity for oxygen.

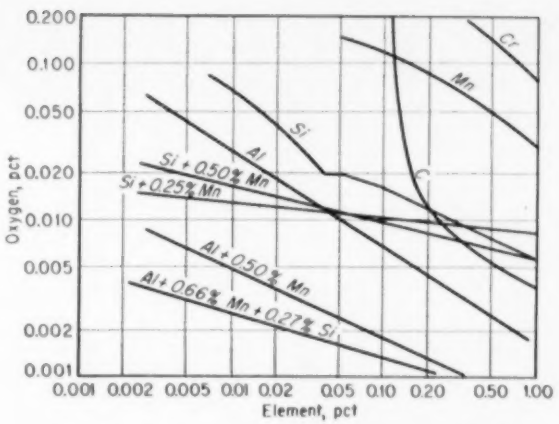

Fig. 3—Deoxidizing power of silver, manganese, aluminum, and combinations of these elements, as well as carbon and chromium are shown at 1600°C.

Deoxidation occurring after pouring is more complete and probably results in the same final residual oxygen contained in the solid steel, for a given grade, regardless of how it was deoxidized in the furnace. It occurs independently of the steelmaker, according to the natural low solubility and evolution governed by the change of temperature.

One question stands out: "Should steel be deoxidized in the furnace more completely, leaving possible low residual oxygen for self-deoxidation or should heats be tapped with high residual oxygen which would cause more intensive self-deoxidation?" Practice appears to favor high residual oxygen for cleanliness of steel, good macro, and consistently high physical properties, particularly those taken from forgings in transverse direction.

Is there a relationship between deoxidation and degasification of steel? Laboratory and operational men have attacked the problem of gases in steel, particularly hydrogen. Hydrogen causes unsound ingots and castings as shown in Fig. 4. Percentage of unsound heats in a melting shop depends largely on the variety of grades made and the degrees of alloying. Generally, the shop making a certain tonnage of average analysis containing 15 pct alloying elements will be more involved with gasiness than the shop where analysis averages 6 pct.

The belief that wet raw materials are the source of hydrogen is sound. But, can steel plants dry, or remove rust and oil from scrap? There have been cases where scrap and other material conditions were almost ideal and yet ingots were unsound. Investigations have disclosed that iron absorbs four to five times as much hydrogen when it reaches the melting point that it does during total period of heating from room temperature to melting point. If temperature is increased over the melting point absorption of hydrogen by liquid iron occurs more rapidly.

If there is any period when metal absorbs hydrogen in larger quantities it is during the melting of scrap. Moisture enters the furnace from various sources. However, where scrap and other material contain practically no moisture, the atmosphere is the only source.

Fig. 4—Hydrogen, one of the problem gases in steel, accounted for this unsound ingot. Sources of hydrogen are wet raw materials and the atmosphere.

Observations, experiments, and conclusions presented concern conditions encountered when atmospheric humidity was high. All heats were made under high partial pressure of water vapor in the air. Volumetric percentage of moisture in the air can be found from formula based on Dalton's law of partial pressures.

A typical winter condition might be where temperature is 40°F; relative humidity, 45 pct; and barometric pressure, 735 mm. A summer day might show temperature of 90°F; relative humidity, 80 pct; and barometric pressure, 740 mm. From Dalton's law it can be seen that there is 0.38 pct moisture during this particular winter day, and about 4.1 pct during the summer. During summer, there may be times when the air contains ten times more moisture than it does during winter.

Fig. 5 shows that humidity may vary as much as 100 pct within a matter of hours. Experience has shown that in electric steelmaking summer is the most critical period of the year for difficulties caused by increased tendency to gasiness. For certain scrap charges and melting procedures a quantity as low as 1.5 pct moisture in the air is dangerous. It may be taken as a general rule that when the result of multiplication of temperature and humidity is 4800 or higher, all precautions should be taken with grades susceptible to gasiness. This applies particularly to heats of the *remelt* type.

Chemical composition of scrap plays an important part in daily practice. Higher the percentage of alloy elements in scrap, the greater the possibility of making unsound heats. Some alloy steels made on virgin charges practically never give unsound heats. If, however, alloy steel is made with a charge containing alloy scrap, occasionally unsound metal results. It would appear that saturation by gas occurs during the melting period, because refining and finishing stages of melting are much alike in both cases.

Moisture entering the furnace in contact with iron or any metallic ingredient in steel is bound to react this way:

$$H_2O + Fe_{liq} = H_{2\,in\,Fe} + FeO \qquad [1]$$

The equilibrium constant K of this reaction is as follows:

$$K = \frac{P_{H_2O}}{P_{H_2O(FeO)}} = \frac{P_{H_2O}}{P_{H_2}}\,(FeO)\ max \qquad [2]$$

It appears from equation 2 that the ratio P_{H_2O}/P_{H_2}, at a constant temperature, is a function of the degree of deoxidation of the metal, the FeO content. In the presence of iron saturated by its oxide at the concentration (FeO) max, the ratio P_{H_2O} to P_{H_2} must be constant, which in this case depends solely on the temperature.

Under ordinary conditions during the melt down stage, the metal is not saturated with FeO and hence the ratio of P_{H_2O}/P_{H_2} increases in continuous manner. Thus, the hydrogen evolution occurs more or less intensively. The free hydrogen acts on bare scrap at the electric arc temperature and saturates the scrap.

Important conclusions for practical steelmaking can be drawn from equation 2:

1-Higher the moisture content in the furnace atmosphere the more hydrogen released if other conditions such as temperature and quantity of iron oxide dissolved in the fluid bath are constant. This indicates that certain standard melting methods giving good results during low humidity periods may be disappointing when humidity is high, if applied factor of temperature and iron oxide is not changed.

2-Quantity of iron oxide dissolved in the fluid bath determines the evolution of hydrogen. The more iron oxide dissolved, the less hydrogen released.

Analysis of unsound heats over a period of years disclosed that about 60 pct of these heats were made as first heats after a weekend; heats made on cold lining. Equation 1 was referred to as the source of the continuous evolution of hydrogen in search of reasons why cold melted heats were more susceptible to gasiness. This evolution cannot be halted if there is not enough FeO in the system. A sufficient quantity of FeO must be dissolved in the bath. This can be done only by a higher temperature or hot melt-down, when all other conditions are constant.

If the temperature on melt-down is high enough this reaction cannot only be stopped but reversed. Hydrogen which once went into solid solution with the metal during the cold part of the melting period can be eliminated as H_2O a short time later, when conditions of higher temperature are met. This may take place at the end of the melting period or shortly afterward, depending on quantity of hydrogen introduced during melting and the amount of oxygen dissolved during the period of high temperature action.

It was also found that the presence of alloy elements in the remelt type charge worked against oxygen dissolution because most of these elements have a higher affinity for oxygen than iron. Action of alloy elements relies upon continuous decomposition of iron oxide created during melting. Thus, they facilitate the occurrence of equation 1 to its right side.

Convincing proof was discovered during the course of experiments. Certain grades of steel containing from 20 to 25 pct alloy elements in the final analysis and containing about 95 pct of these elements in the charge were melted by this method:

After the charge was melted, additional lime was added and the slag began to be reduced. When it reached a satisfactory appearance, the alloy test was taken and the slag-off operation followed. The routine was modified by taking soundness tests; first test immediately after the charge was melted and a second test before the reducing process was started. Some of the first tests appeared to be unsound. Upon analysis they showed from 0.10 to 0.20 pct Si. Normally, Si in such quantities assured sound metal. Within the next 30 to 40 min metal temperature was raised by 80° to 100°F and a second test taken. Tests showed sound metal despite drop of Si content of 0.07 to 0.10 pct. This was considered sufficient proof of the assumption that by heating up relatively cold metal and dissolving a certain quantity of oxygen in the fluid metal, a certain amount of hydrogen could be removed from the fluid bath, probably in the form of H_2O. This conclusion applied to 60 pct of the heats investigated. However, 40 pct remained showing unsound metal before tapping despite seemingly being melted in the regular manner. It was revealed that almost all of the 40 pct were worked out cold in further stages of the melting procedure. Reasons for cold runs were found to be:

1-In the course of practice, heats which show relatively hot metal on the melt-down test, have not melted completely, some scrap being left on the bottom. Even experienced operators sometimes fail to discover the relatively thick uniform layer of solid metal covering the lining and almost of perfect bottom shape. When the voltage is switched to low, the upper fluid part of the charge becomes cold. When it remains in this condition for some time, it almost always gives unsound metal before the tap.

2-Properly melted-down and even reduced heats can be spoiled during the period after the operator sends the alloy test, and after slagging-off adds new refining slag. During this period of 40 to 80 min of waiting for analysis results some operators do not take proper care of the bath temperature. Slag thins, heat supplied by the electric arc reflexes to the roof, and the bath becomes cold. When the analysis arrives, final additions of ferroalloys cool the bath further, and when everything is adjusted the metal appears too cold to tap. Fast heating of the metal brings the temperature to a level high enough to pour ingots—and usually creates a dangerous condition that is one of the factors contributing to unsound metal.

3-*Diluting* the heats results similarly in cooling the baths. One or more alloy elements may come up too high. Diluting the heat by charging a quantity of solid scrap would appear to save the analysis. However, if the heat becomes too cold and is tapped out without special temperature treatment, the metal may be unsound.

4-Irregular heats, the so-called long heats, usually submitted to variable temperatures, are subject to hydrogen saturation.

The opinion that hot worked out heats, rather than cold ones, have a tendency to be wild, needs correction. The deciding factor seems to be the quantity of oxygen dissolved in steel. If metal temperature is increased and elements of high oxygen affinity are added at the same time, there seems to be every chance of hydrogen saturation of the fluid metal. However, if metal temperature and residual oxygen in the metal is increased at the same time, hydrogen elimination occurs so definitely that some heats which appear unsound may be saved by heating them to a certain temperature.

Hydrogen and oxygen, both contained in the fluid metal and dissolved in high quantities with the increase of temperature, reach a certain temperature at which the oxygen is dissolved in much higher proportions than the hydrogen. The reaction between Fe and H_2O is not only halted, but the direction of this reaction is changed, with oxygen attacking hydrogen and eliminating it as H_2O.

Occasionally, conditions preventing saturation of metal by hydrogen during the melting or refining periods are not maintained and the heat proves unsound when ready to tap.

When no means existed for correcting such a heat it was tapped and scrapped. Neutral gases, used in recent years, when blown through saturated metal are supposed to remove hydrogen. Mechanical action of the molten metal caused by gas passing through under pressure is believed to be the reason for hydrogen removal.

Years ago, steelmakers noticed that heats subjected to a boiling period utilizing iron ore, showed a considerably lower percentage of unsound heats. Neutral gases cause the same mechanical turbulence of the fluid bath as do ores.

Differing results were obtained with the use of neutral gas. It seemed to be a big step forward in saving unsound heats. Again, in the case of boiled heats, the quantity of residual oxygen left in fluid bath after boiling seems to determine the degree of degasification and the susceptibility of the metal to gasiness. The higher the residual oxygen at the end of boiling, the better the degasification and the less chance of hydrogen saturation in the next stages of melting. It means that in practice a heat containing 0.60 pct C and 0.50 pct Mn on the melt-down test, boiled down to 0.25 pct C and 0.35 pct Mn will result in metal more susceptible to gasiness than the same heat boiled down to 0.10 pct C and 0.10 pct Mn.

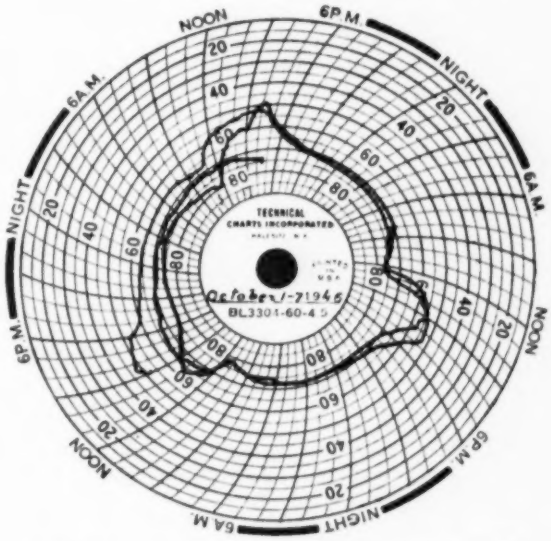

Fig. 5—Chart shows that humidity may vary as much as 100 pct within a matter of hours.

Fig. 6—Fracture tests of heats of high speed steel before and after oxygen injection are shown. Oxygen plays the dominant role in removing hydrogen.

One question arises. Is the mechanical action of boiling a dominating factor in removing hydrogen from the fluid metal or is it the presence of excessive oxygen which reacts with hydrogen in the same way as it does with carbon, silicon, or manganese while mechanical action of the fluid metal is only coincidental?

It might be said that the reason for hydrogen removal during boiling is its reaction with oxygen. This seems to be as true as the idea that hydrogen removal occurs purely because of mechanical action.

Referring again to the problem of the effect of neutral gas bubbling, it is necessary to point out that these findings show that the application of nitrogen, for example, was not always successful.

In searching for factors determining the more positive effect of flushing by neutral gas, it was noted that heats of higher temperature at flush time were easier to desaturate of hydrogen. Tests were then made by heating unsound heats 50° to 100°F over tapping temperature, followed by bubbling. Percentage of saved heats increased, and about half as much nitrogen was required than when flushing without regard to metal temperature. From the success of desaturation of hydrogen under the aforementioned conditions, it was natural to evolve back to the theory that the mutual quantitative ratio of oxygen-hydrogen in the fluid metal was a factor of at least equal importance to mechanical action caused by blowing neutral gas.

Going further, this procedure was applied: When a heat ready to tap proved unsound a quantity of iron ore was thrown into the furnace and voltage increased. As a result, silicon was lost quickly. When the heat reached the desired temperature, blowing began. Elimination of hydrogen was rapid and easy.

After determining that oxygen injection before blowing helped to desaturate the fluid metal, the next step was to find out how important oxygen was in the desaturation process. What was most important, mechanical action of the bath caused by neutral gas or oxygen injection? To answer this a five-ton furnace was employed. When a heat ready to tap proved unsound, four to six shovels of iron ore were placed in the furnace and voltage increased until bath temperature reached approximately 100°F higher than regular tapping temperature. The bath was kept at this temperature for 30 to 40 min, and then the voltage was turned to the lowest point. Slag was reduced with a simultaneous introduction of 0.10 to 0.15 pct Si. When normal bath tapping temperature was reached, the heat was checked for soundness. Four of five heats treated this way proved to be sound and were tapped with nitrogen flush. Fig. 6 shows the fracture test for one of these heats before and after the aforementioned oxygen injection was applied.

Steel was of high speed grade, type 18-4-1. Temperature of the heat was raised to 3160°F. The entire desaturating procedure lasted about 1 hr. It appears that oxygen rather than mechanical action of the bath plays the dominating role in removing hydrogen.

In another supporting case a heat containing 0.10 pct C and 17 pct Cr was worked out too cold. Conditions on the melting log made it possible to predict that the heat would be unsound before tapping. This was confirmed by the test. The combination of heating, oxidizing, and blowing corrected the heat. Seventeen 1400-lb ingots were poured with a 2¼ lb piece of aluminum added to molds No. 6 and 11. Only the two with aluminum settled poorly, the rest were successful.

This would indicate that the aluminum bound the residual oxygen before it reacted with oxygen. The latter was left free to precipitate and caused bleeding. It is also indicated that hydrogen is a stronger reducer than silicon because ingots containing silicon settled normally. There was enough residual oxygen to combine with hydrogen as H_2O before the oxygen was combined by silicon.

Another case throws light on the behavior of hydrogen in the basic electric furnace. A heat of analysis 0.78 pct C, 8.5 pct Mo, 15 pct W, 4 pct Cr, and 1.10 pct V almost at the tapping stage showed a high degree of unsoundness. The corrective treatment was heating the bath to about 100°F over the regular tapping temperature, adding ore to the slag to accelerate the silicon elimination, and applying nitrogen flush. One electrode went out of order after 10 to 15 min of heating, switching off and on at about 5 to 6 in. distance over its regular position. To correct this, electricians had to keep power on while working in the transformer room. Power remained on for about 2 hr before trouble was eliminated. The bath reached 3200°F after the first hour and vigorous boiling began. It lasted through the second hour. From observed intensity of boil a carbon loss at the rate of 0.30 pct per hr could be expected.

When the trouble was rectified, electrodes were raised to cool off the bath. At 3060°F boiling disappeared and C test was sent to the laboratory. Carbon was reported at 0.78 to 0.79 pct, surprising after an hour's vigorous boiling. Repeated tests showed carbon at 0.78 to 0.80 pct. Slag was reduced when the bath reached tapping temperature, and after silicon addition a soundness test was taken. The metal was perfectly sound. The heat tapped out showed final carbon 0.80 pct. Only explanation possible for intensive boil without loss of one point of carbon would be: Raising temperature of this highly hydrogen saturated heat to an unusually high level increased residual oxygen to such an extent that visible and intensive reaction was caused between both gases. It is probable that the result of the reaction was production and evolution of H_2O.

These examples suggest that in making alloy steels with more or less high susceptibility to gasiness melting procedures should be attuned to maintaining the highest possible residual oxygen during the entire melting. Generally, this means hot melting, hot working out of the heat, and in some cases, hot tapping.

Vacuum Dezincing of Desilverized Lead Bullion

by T. R. A. Davey

THE possibilities of separating and purifying metals by high vacuum distillation were examined by Kroll.[1] He suggested vacuum treatment for the removal of zinc from the lead produced after Parkes desilverizing. The St. Joseph Lead Co. developed the first commercial vacuum dezincing process at their Herculaneum refinery, as described by Isbell.[2] The Broken Hill Associated Smelters at Port Pirie, Australia, has, after several years of pilot plant operations and fundamental investigations, developed a continuous process, which will be described briefly in a forthcoming publication.[3]

As the full-scale continuous vacuum dezincing plant at Port Pirie is still experimental, publication of full practical details of the plant will be deferred until the unit is operating as a normal part of the continuous refinery. This paper deals only with theoretical aspects of vacuum distillation processes, with particular reference to vacuum dezincing. The method of mathematical analysis is of general interest as it may be applicable to other metallurgical separations which have been investigated recently.[4-6]

Evaporation Processes

At about atmospheric pressure, or higher, most liquids possess a boiling point—a temperature at which any heat put into the liquid is absorbed only as latent heat, not as specific heat. If a steady heat input is supplied, the liquid's temperature rises to this value, then remains constant while bubbles of vapor form beneath the surface. The rate of evaporation is determined solely by the rate of heat transfer to the liquid; the temperature of boiling is determined by the partial pressures of the volatile constituents in the liquid, and the total pressure above the surface. If the rate of heat transfer to the liquid is increased, the temperature remains constant, and the rate of boiling increases.

When evaporating metals under vacuum, however, the partial pressures concerned are generally so small that boiling does not occur, because at even a fraction of a millimeter below the surface the hydrostatic pressure is usually too great to permit the formation of a pocket of vapor. In addition, the high thermal conductivity of metals tends to prevent the local superheating which is necessary for bubble formation.[7] Although this effect is doubtless also exerted when boiling metals at higher pressures, the magnitude will be less because the degree of superheat required to form bubbles is very much less at the higher temperatures involved.

Under vacuum, therefore, evaporation of volatile constituents takes place only from the exposed surface, and the rate of evaporation depends upon the surface area, the surface concentration of volatile constituents, the surface temperature, and the partial pressures of volatile constituents immediately above the surface. If the heat input is raised above a certain level, the effect is not to increase the evaporation rate at constant temperature, but to raise the temperature of the liquid until at some higher level an increased rate of evaporation (and thus of latent heat absorption) again balances the heat input rate.[7]

Many substances (including metals) have a very large intrinsic evaporation rate at quite low temperatures—far below their normal boiling points. However, at atmospheric pressure, the large numbers of atoms evaporated are almost completely deflected back into the liquid (or solid) surface by air molecules. Thus the back condensation rate is practically equal to the gross evaporation rate, and the net evaporation rate is practically zero.

It can therefore be seen that an overall distillation rate depends not only upon the intrinsic evaporation rate, but also upon the ability of the volatile atoms to move away from the evaporating surface. This movement is facilitated by the provision of a condensing surface close by.

Vacuum Distillation: The function of the vacuum above the evaporating surface is to remove foreign molecules, so that the chances of deflection of an evaporated atom back into its source are reduced. When the residual gas pressure is reduced so far that the evaporated atoms have a high probability of reaching a nearby condensing surface without suffering collision with a foreign molecule, the state of affairs is termed "molecular distillation." This process is practiced commercially today for the purification of numerous organic chemical products of high unit value, but not, to the writer's knowledge, for any metallurgical separation.

When the degree of vacuum produced in a still is not sufficient to promote molecular distillation, then the evaporated molecules must diffuse through the

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The word bullion as used in this paper refers to impure lead.

The Transactions papers appearing in the Journal of Metals during 1953 will subsequently appear in AIME Transactions Volume 197, and may be permanently referenced to that volume.

Table I. Values of Constants

Temperature, °C	DP	$10^2 xa$	$10^2 xb$*	c†	r
580	0.89	1.62	2.76	0.171	0.381
600	0.93	1.60	2.82	0.173	0.279
620	0.96	1.58	2.86	0.175	0.209
650	1.02	1.55	2.94	0.178	0.138

* Assuming distillation space $L = 30$ cm.
† Assuming $T_c = 420$°C; if $T_c < 300$°C, $c < 0.002$.

distillation space, from evaporating to condensing surfaces. There will then be a partial pressure of volatile atoms above the evaporating surface, which produces some back condensation. A net evaporation rate results, smaller than the intrinsic or gross rate. Under steady state conditions this evaporation rate is equal to the rate of migration of atoms across the distillation space, and equal to the rate of condensation.

If the construction of the still is such that obstruction is offered to the flow of vapor by the vessel walls, pipe lines, or baffles, then of course mass flow is permitted, and the total pressure is different in different parts of the distillation space. If such obstructions do not exist, then obviously the total pressure must be uniform throughout the distillation space.

Vacuum Dezincing

It can be shown that in vacuum dezincing as practiced today the distillation proceeds by diffusion of zinc atoms from the bullion surface, through the stagnant atmosphere, to a nearby condensing surface. The designs of apparatus insure that there is no resistance to the flow of zinc vapor apart from that due to the residual gas pressure.

The bullion prior to treatment is just above its freezing point, and after dezincing will be refined at about 450° to 500°C. It is therefore conveniently treated in the liquid state. In order that the free surface exposed to vacuum shall not be mechanically obstructed, the metal surface should be clean, i.e., free from dross. Since distillation is much more rapid than diffusion of zinc through molten lead, vigorous agitation is required to prevent surface impoverishment in zinc, and also to prevent a fall of temperature at the surface due to radiation loss and provision of the latent heat of vaporization of zinc.

The St. Joseph batch operation employs a mechanical stirrer to produce agitation. The Port Pirie continuous operation utilizes a falling film* of bullion, which flows turbulently, and does not require mechanical agitation.

* The term "film" is not meant to be understood in the strict physical sense of lamellar flow, but simply in the sense of a thin flowing stream.

Nature of Distillate: In a batch process the distillate may conveniently be condensed in solid form. For a truly continuous process the distillate should be condensed either as a liquid, or else on to a liquid vehicle, so that in either case it may be removed from the still without breaking the vacuum. On the other hand, a continuous process may also be operated to produce solid distillate, if removal of the distillate is accomplished so rapidly that the vacuum is broken for a negligibly small period.

In order that a solid distillate shall not occupy too great a volume in the vacuum chamber, it should be condensed in a compact (dense) form. The observations of St. Clair and Spendlove,[7] on the condensation of zinc, and Betcherman and Pidgeon,[4] on the condensation of magnesium, are in general agreement with our own, which may be summarized as follows:

> Low rates of distillation and high residual gas pressures tend to produce loose clusters of dendritic crystals; with good vacuum (less than 100 microns) tightly packed columnar crystals are produced, the mass when fractured appearing very similar to a broken slab of cast zinc; with very high rates of distillation, with high lead content, or with high temperatures of condensation (as when the distillate layer is very thick) the edges of the crystals appear rounded, and show evidence of having been liquid—individual crystals tend to merge into a large mass, the surface of which may exhibit large crystals as on a slowly cooled cast bar.

Condensation phenomena will not be discussed further; for the practical operation it is necessary only to know that at pressures less than about 150 to 200 microns, with a condensate surface less than about 6 in. from the water-cooled surface, the condensate consists of closely packed columnar crystals.

The amount of lead distilling over with the zinc increases with temperature, because the relative difference in vapor pressures becomes less as the temperature is raised. The best separation is obtained at the lowest temperatures, as Kroll has observed.[1] However, the zinc recovered from desilverized bullion is used again for desilverizing, so that contamination with lead is of no consequence. The amount which occurs in practice is less than 10 pct, which represents less than 0.05 pct of the lead treated, so is not a very great circulating load.

It is desirable that the condensate be as free as possible of oxygen. On melting the distillate for solution in lead, not only is any zinc oxide present wasted, but also its removal as dross incurs further loss of entangled metallic zinc and lead.

With an indicated vacuum of less than about 150 to 200 microns, very little zinc is oxidized, and the distillate is very shiny in appearance.

Rate of Distillation

The rate of distillation is of paramount importance, as it determines whether or not the process will be economic. By considering the three parts of the process—evaporation, migration, and condensation—the distillation rate may be determined. In the first analysis the presence of lead vapor may be neglected.

Consider unit area (1 sq cm) of evaporating surface, distillation space, and condensing surface, the temperature of evaporating surface and vapor being T (°K) and of condensing surface T_c (°K), the distillation space being L (cm) across, the pressure being P (mm Hg) throughout. Let the partial pressure of w pct Zn in the bullion at the evaporating surface be p', in vapor above the evaporating surface be p_1, in vapor above the condensing surface be p_2, and in the condensing surface be p_c (all mm Hg).

Zinc diffuses through an atmosphere of nitrogen, since any oxygen present is quickly combined as zinc oxide, and removed from the atmosphere. If there are no air leaks in the system, and the vacuum line off-take is adjacent to the condensing surface, then the partial pressure of nitrogen immediately

above the condensing surface will be V (mm Hg), the recorded vacuum.

At any instant the total pressure at all points in the distillation space is constant, and equal to the sum of the partial pressures of zinc and nitrogen, then,

$$P = p_z + V \qquad [1]$$

From Langmuir's equation for absolute rates of evaporation,

$$E = a(p' - p_i) \qquad [2]$$

$$C = ap_z - kp_c \qquad [3]$$

where $a = \dfrac{0.472}{\sqrt{T}}$ and $k = \dfrac{0.472}{\sqrt{T_c}}$ for zinc.

Using the methods of Lewis and Chang[8] for isothermal diffusion of zinc vapor through nitrogen,

$$M = b \ln \frac{P - p_2}{P - p_1} \qquad [4]$$

$$= b \ln \frac{V}{V + p_z - p_i} \qquad [4a]$$

where $b = \dfrac{0.796DP}{TL}$.

Values of DP—independent of all other terms except temperature—are given in Table I.

Placing $E = M = C$ in Eqs. 2, 3, and 4a, the following is obtained:

$$p' = V + c + \frac{2E}{a} - V \exp\left(-\frac{E}{b}\right) \qquad [5]$$

where $c = \dfrac{kp_c}{a}$

This is the fundamental equation relating E, the net distillation rate, to p', the partial pressure of the volatile element in the distilland (the material to be distilled), with the constant terms V (measured vacuum), a (depending only on temperature and the distilling element's vapor pressure and molecular weight), b (depending on temperature, length of distillation path, and the diffusivity of distillate molecules through the inert atmosphere molecules), and c (depending on condensing temperature and the other factors influencing a).

If the ratio between w and p' be represented by r, then,

$$w = r\left[V + c + \frac{2E}{a} - V \exp\left(-\frac{E}{b}\right)\right] \qquad [5a]$$

where $r = w/p'$.

In the process being considered the behavior of zinc atoms in diffusing is likely to be adiabatic rather than isothermal, as indeed previous writers have assumed.[7] However, the expression then obtained is very complex, and tedious to manipulate mathematically. It has been evaluated and compared with Eq. 5 for sufficient values to indicate that in the region of practical interest the difference between isothermal and adiabatic diffusion does not introduce errors greater than about 10 pct.

An approximation to Eq. 5a may be made for the values of constants applying in practice, since the exponential term is then negligible—much less than 1 pct of the right-hand side of Eq. 5a,

$$E = \frac{a}{2r}(w - rV - rc) \qquad [5b]$$

provided that $w > r\left(\dfrac{16b}{a} + V + c\right)$.

A further approximation may be made if the condensing temperature is less than 300°C, since then c may be neglected. Thus for conditions of cold condenser (designated "C.C." in the figures),

$$E = \frac{a}{2r}(w - rV) \qquad [5c]$$

Practical Application

The equations just derived will be considered as they apply to the apparatus of the St. Joseph batch process, and also to the apparatus of the Port Pirie continuous process, although strictly speaking it is not applicable in the latter case because P is not constant throughout the distillation space. The limitations will be discussed more fully in a later publication.

Batch Process: If the rate of evaporation from the surface area A (sq cm) of B (g) of bullion is E (g cm^{-2} sec^{-1}) at time t (sec) after the start, when the zinc concentration is w (wt pct) and the concentration of zinc changes by $-dw$ pct in time dt sec, then,

zinc evaporated = zinc lost from bullion,

i.e., $EAdt = -\dfrac{Bdw}{100}$ g

$$\text{or} \quad t = \frac{B}{100A}\int_{w_f}^{w_i} \frac{dw}{E} \text{ sec} \qquad [6]$$

$$= 13.2 \int_{0.05}^{0.95} \frac{dw}{E} \text{ sec} \qquad [6a]$$

for the St. Joseph plant conditions.

Nomenclature

Although these units must be used in equations, in the text temperatures are given in degrees centigrade and pressures in microns.

Symbol	Dimensions	Explanation
A	Sq cm	Area of evaporating surface = 8.0×10^4 in St. Joseph plant
a	—	Constant in Eqs. 2, 3, 5, 7, 8, and 10. See Table I
B	Grams	Quantity of bullion = 1.055×10^5 in St. Joseph plant
b	—	Constant in Eqs. 4, 5, 7, and 10. See Table I
C	G cm^{-2} sec^{-1}	Rate of condensation
c	—	Constant in Eqs. 5 and 10. See Table I
D	Cm^2 sec^{-1}	Maxwell's diffusivity
E	G cm^{-2} sec^{-1}	Rate of evaporation or distillation
F	Tons per hr	Bullion flow rate
k	—	Constant in Eq. 3
L	Cm	Distance across distillation space
M	G cm^{-2} sec^{-1}	Rate of migration of vapor
P	Mm Hg	Total pressure in distillation space
p'	Mm Hg	Partial pressure of zinc in evaporating surface of bullion
p_1	Mm Hg	Partial pressure of zinc above evaporating surface
p_2	Mm Hg	Partial pressure of zinc above condensing surface
p_c	Mm Hg	Partial pressure of zinc in condensing surface
r	—	Ratio w/p'
T	°K	Temperature of evaporating surface, and of vapor above evaporating surface
T_2	°K	Temperature of vapor above condensing surface
T_c	°K	Temperature of condensing surface
t	Sec	Time in seconds after start of a batch distillation process
u	—	E/b
V	Mm Hg	Vacuum, or residual gas pressure
w	—	Weight percent zinc in bullion
Subscript i	—	Initial
Subscript f	—	Final

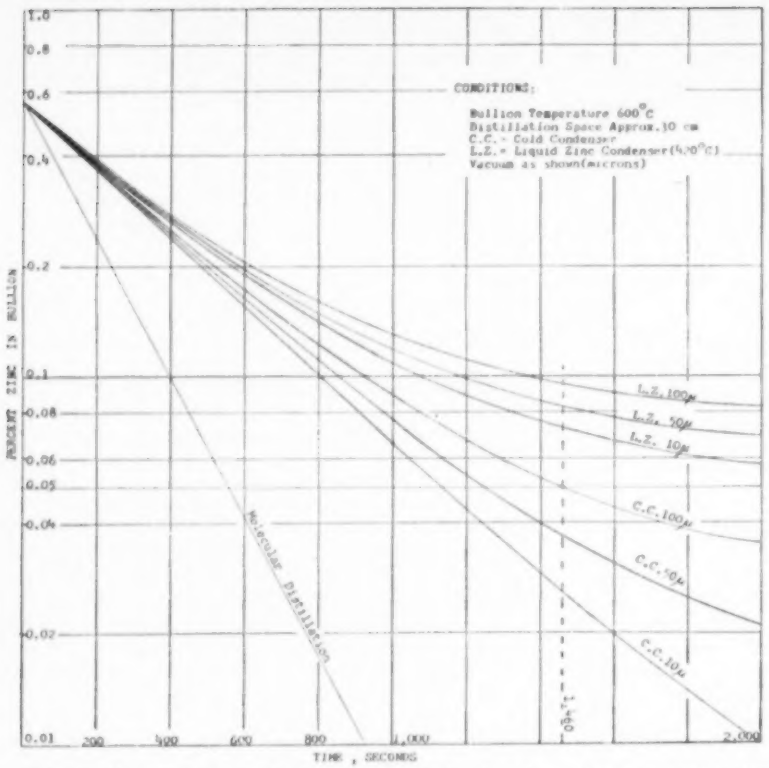

Fig. 1 — Time-elimination curves.

Substituting Eq. 5a or 5c in 6a, the following is obtained:

$$t = \frac{26.4r}{a} \ln \frac{E_i}{E_f} + \frac{13.2rV}{b} \int_{u_f}^{u_i} \frac{e^{-u}}{u}\, du \qquad [7]$$

where $u = E/b$

or $$t = \frac{26.4r}{a} \ln \frac{w_i - rV}{w_f - rV} \qquad [7a]$$

As a matter of interest, the corresponding equation for molecular distillation is

$$t = \frac{13.2r}{a} \ln \frac{w_i}{w_f} \qquad [8]$$

Molecular distillation cannot occur unless the distillation space is reduced to approximately 0.2 cm with a vacuum of 100 microns, as compared with approximately 30 cm obtaining in practice; or the pressure is reduced to less than 0.7 microns with a distillation space of 30 cm.

It is of interest to consider Eq. 7a more closely: the time of treatment is shown to depend upon initial and final zinc content of bullion; residual gas pressure (or vacuum, V); and temperature of bullion, which enters the constant term a. It is, however, independent of the distillation space, L, which enters only into the term b and is not significant in the practical range (down to 0.05 pct Zn). L becomes significant only at values of w below 0.04 pct Zn. Eq. 7a is also independent of the condenser temperature provided it is below 300°C. If T_c exceeds 300°C then the full Eq. 7 must be used.

Some evaluations of Eq. 7 are presented in Fig. 1, for a bullion temperature of 600°C, and vacua of 10, 50, and 100 microns. For comparison, the rate of molecular distillation is also shown (Eq. 8) and further evaluations of Eq. 7 on the assumption that the condenser is at the melting point of zinc, 420°C.

The value of r has been determined using Kelley's vapor pressure data for pure zinc,[9] and Lumsden's expression[10] for the free energy of mixing of zinc and lead, after checking its accuracy against the vapor pressure measurements of Jellinek and Wannow[11] together with the Zn-Pb phase diagram

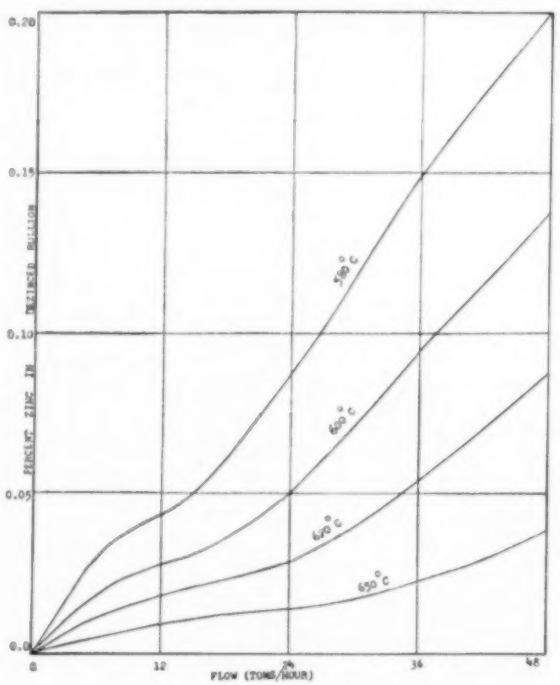

Fig. 2—Effect of bullion flow rate.

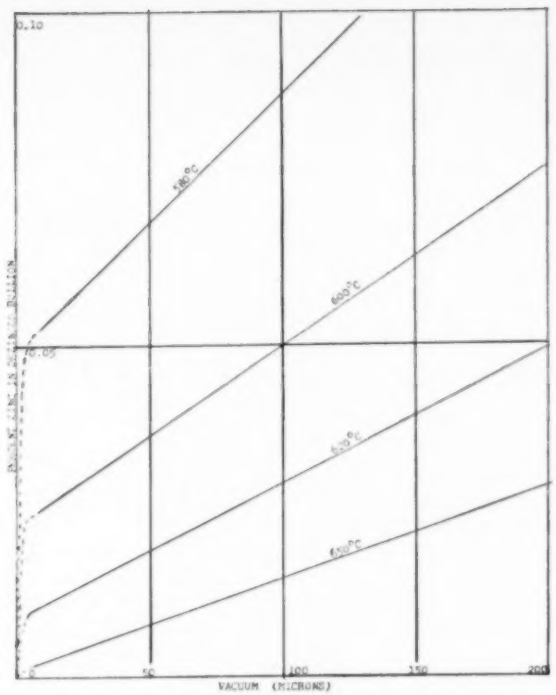

Fig. 3—Effect of vacuum.

of Waring et al.[12] Values of a, b, c, and r for a variety of bullion temperatures are given in Table I.

It is evident, from Fig. 1, that under the normal St. Joseph operating conditions, treatment time should be 1,460 sec, whereas in practice it is about 5 hr, or 18,000 sec. The discrepancy could be due to one of two causes: 1—concentration of zinc, or the temperature, may be lower at the bullion surface than in the bulk; and 2—some zinc vapor may condense before reaching the condensing surface, fall back into the bullion bath, and require re-evaporating. Although the first factor certainly operates to some extent, its effect is small compared with that of the second. This point will be discussed subsequently.

Continuous Process: In identical manner to the derivation of Eq. 6, it is found that:

$$\frac{1}{F} = \frac{2.82}{A} \int_{w_f}^{w_i} \frac{dw}{E} \text{ hr per ton} \qquad [9]$$

or

$$\frac{1}{F} = \frac{5.64r}{Aa} \ln \frac{w_i - rV - rc}{w_f - rV - rc} + \frac{2.82rV}{Ab} \int_{u_f}^{u_i} \frac{e^{-u}\, du}{u} \qquad [10]$$

The area A required to dezinc any flow of bullion (F ton per hr) may then be determined by insertion of appropriate values of the constants. At a bullion temperature of 600°C, a vacuum of 100 microns, and with a cold condenser, zinc is removed from 0.56 to 0.05 pct if approximately 0.34 sq ft of evaporating area is provided for each ton per hr of bullion flow.

Fig. 2 shows the manner in which variation in flow produces variation in dezinced bullion assay, assuming a constant 0.56 pct Zn in desilverized bullion. In this evaluation of Eq. 10, A has been taken as 8.1 sq ft (7,500 sq cm), when a bullion flow of 24 tons per hr is dezinced to 0.05 pct Zn at $T = 600$°C, $V = 100$ microns.

Fig. 3 shows how the dezinced bullion assay varies with vacuum for a variety of bullion temperatures with a cold condenser.

Fig. 4 shows the variation in dezinced bullion assay with bullion temperature, for a variety of vacua, for liquid zinc condensation (at 420°C) as well as cold condenser. It is apparent that in order to obtain the same operating results with a liquid zinc condenser as with a cold condenser, in the same size of apparatus, the bullion temperature should be 30° to 35°C higher.

The theoretical limit of zinc removal shown in Fig. 4 is imposed by the fact that at the concentrations and temperatures shown the partial pressure of zinc in bullion equals the vapor pressure of zinc at its melting point—154 microns.[9]

The agreement between calculation and practice has been found to be reasonably good in the Port Pirie falling-film type of apparatus, both as to the absolute magnitude of the distillation rate and as to the dependence of results upon vacuum and temperature and independence of distillation space. The dependence on rate of bullion flowing through the unit is not demonstrated, however, because the area available for evaporation is automatically varied with the bullion flow.

It should be mentioned that Figs. 3 and 4 apply as well to a batch process as to a continuous process, provided that precondensation of zinc vapor does not falsify the results.

Comparison With Other Theoretical Work

Carman[13] presented a mathematical description of vacuum distillation processes in 1948. As his work has been quoted recently[14, 15] it will be of interest to compare his results with the presentation here.

Carman presents an equation for evaporation exactly as Eq. 2, but his analogue of Eq. 4 is:

$$M = b \ln \frac{P - p_c}{P - p_i} \qquad \text{[Carman 1]}$$

It is seen that Carman assumes the partial pressure of zinc above the condensing surface p_s to be equal to p_c, whereas it is quite evident that p_s equals

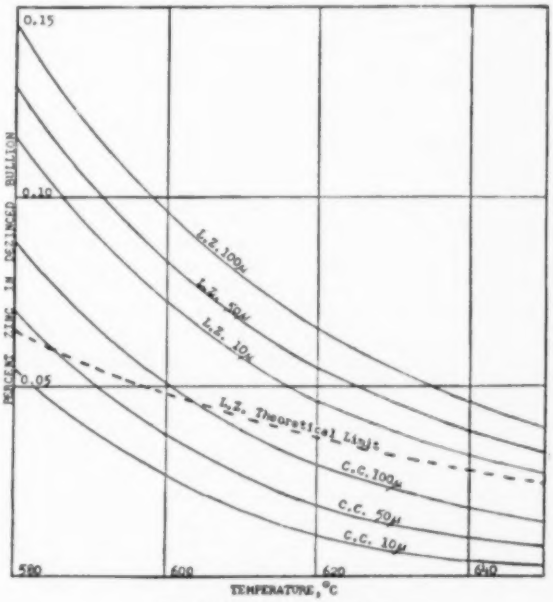

Fig. 4—Effect of temperature.

p_v only if the rate of condensation is zero. His expression for M is therefore much too high because in general p_i is much greater than p_v.

Further errors of implication arise through confusion of P, the total pressure in the still, with V, the residual gas pressure. These will not be discussed here beyond stressing that P may be many times greater than V, and varies during a batch dezincing operation from roughly 1000 microns initially to about 130 microns finally, whereas V remains constant, after the initial pump-down period, at 50 to 100 microns.

Richardson[10] makes the same confusion, in writing of the St. Joseph process: "In the actual process the pressure falls to 0.05 mm in the first two hours of distillation, corresponding to rapid removal of the zinc to 0.1 pct concentration in the liquid." It is clear that V is not affected in any way by p', and hence bears no relation to w.

Precondensation

As Kroll has observed,[1] in metal distillation processes there frequently occurs condensation of vapor into liquid globules before the vapor reaches the condensing surface. In his original vacuum dezincing experiments he placed the condenser below the evaporating bullion, to prevent zinc droplets from falling back into the bullion.

When upward distillation is employed, as in the St. Joseph apparatus, precondensate forms and falls back into the bullion to such an extent that the treatment time is increased approximately twelvefold. When sideways or horizontal distillation is employed, as in the Port Pirie continuous apparatus, precondensate forms to much the same extent, but the liquid globules continue to move away from the (vertical) bullion surface and toward the condenser, presumably in parabolic paths. The distillation rate under such conditions is approximately equal to the calculated rate, although formation of precondensate could be expected to alter the pressure relations assumed for the calculations.

The cause of this precondensation is by no means obvious, since it is not primarily due to fall of temperature of zinc vapor by adiabatic diffusion. The value of T_s may be calculated on the assumption of adiabatic expansion from T, p_i, to T_s, p_v, and it is found that T_s falls below the saturation temperature of zinc vapor only toward the end of the operating cycle.

There is a good deal of evidence that precondensation is connected with lead vapor, which is drawn into the zinc vapor streaming across the distillation space, in much larger quantities than would be the case if lead were distilling alone. The distillation space is therefore always supersaturated in lead vapor, and condensation of lead to liquid globules tends to occur even just above the evaporating surface, without any appreciable fall in temperature. As soon as a liquid phase of lead is formed, zinc can condense on to it, particularly if the globule loses temperature by radiation to the condenser.

Such precondensation amounts to a fractionation of the mixed vapor, and so it would be expected that the percentage lead in the distillate would be greater, the closer the condenser surface is to the bullion. This has been observed in practice. It would also be expected that the lead content of distillate produced by horizontal distillation would increase from the top to the bottom of the (vertical) condenser, since the leady globules tend to hit the condenser lower down. This also has been observed, the lead content increasing from 0.1 to 0.3 pct at the top, to 5 to 10 pct at the bottom.

While not proving the suggested connection between lead vapor and the cause of precondensation, the facts stated above are in complete accord with theoretical expectations.

Calculation of Other Interesting Values

It is of interest to consider absolute evaporation rates, average velocity of zinc atoms, percentage lead in distillate, and the heat effects of vaporizing and condensing zinc.

Absolute Evaporation Rates: Inserting values from Table I in Eq. 5c, for the conditions: $T = 600°C$, $V = 100$ microns, cold condenser, the following is obtained:

$E = 0.0287\ (w - 0.0279)$ g cm^{-2} sec^{-1}.

At $w = 0.56$ pct, $E = 0.0153$ g cm^{-2} sec^{-1}, = 113 lb ft^{-2} hr^{-1}.

or $w = 0.05$ pct, $E = 0.000634$ g cm^{-2} sec^{-1}, = 4.68 lb ft^{-2} hr^{-1}.

Mean Velocities of Zinc Vapor: At p mm Hg pressure, 1 g of zinc vapor occupies

$$\frac{22{,}400}{65.4} \times \frac{873}{273} \times \frac{760}{p} = \frac{7.76 \times 10^5}{p} \text{ cu cm at } 600°C.$$

Now, at 0.56 pct Zn, $p' = 1.950$, $E = 0.0153$, thus $p_i = 1.0$ approximately, hence 0.0153 g cm^{-2} sec^{-1} = 11,900 cm sec^{-1} mean velocity.

Similarly, at 0.05 pct Zn, $p' = 0.186$, $E = 0.000634$, $p_i = 0.146$, hence 0.000634 g cm^{-2} sec^{-1} = 3,400 cm sec^{-1} mean velocity.

These compare with the molecular velocity of zinc vapor, at 600°C, of 54,700 cm sec^{-1}.

Percent Lead in Distillate: At 600°C the vapor pressure of pure lead is 3.8×10^{-4} mm Hg. Assuming that lead enters the vapor to this extent, back condensation being equivalent to that of the zinc, the expected lead content of distillate would be

$$\frac{3.8 \times 10^{-4}}{1.950} \times \frac{207.2}{65.4} \times 100 = 0.062 \text{ pct from bullion}$$

containing 0.56 pct Zn, and

$$\frac{3.8 \times 10^{-4}}{0.186} \times \frac{207.2}{65.4} \times 100 = 0.65 \text{ pct from bullion}$$

containing 0.05 pct Zn.

The figures obtained in practice are somewhat higher than these.

Latent Heat of Vaporization of Zinc: Latent heat of vaporization of pure zinc, according to Kelley,[9] is 28,400 cal per mol at 600°C, and 28,954 cal per mol at 420°C.

Lumsden's expression[10] yields values for the heat of mixing of lead and zinc at 600°C, of 100.6 cal per mol of solution at 0.56 pct Zn, and 9.06 cal per mol of solution at 0.05 pct Zn. Hence the removal of zinc from a solution to reduce its composition from 0.56 to 0.05 pct consumes 5,700 cal per mol of zinc removed.

Thus, to evaporate 1 mol of zinc from lead bullion at 600°C, requires 28,400 + 5,700 = 34,100 cal. Although this figure applies strictly only to removal of zinc between the limits 0.56 to 0.05 pct the variation would not be great if other limits were taken.

The stated reduction of zinc in solution amounts to a molar fraction of 0.016, hence the heat requirement related to bullion is

0.016x34,100

= 545 cal per mol of bullion

= 2.65 cal per g
= 4.78 Btu per lb
= 10,500 Btu per ton

Taking the specific heat of lead as 6.8 cal per mol,[9] the temperature fall of bullion, if heat were not supplied by an external agency while zinc is distilling, would be about 82°C.

If the zinc vapor cools from 600° to 420°C, then condenses to liquid at that temperature, the total heat liberated is 846 + 28,954 = 29,800 cal per mol of zinc, equivalent to 2.325 cal per g of bullion, or 9,200 Btu per ton of bullion.

If the zinc vapor condenses to solid zinc at a temperature of 200°C on the condenser, the corresponding figures are 32,840 cal per mol of zinc, equivalent to 2.64 cal per g of bullion, or 10,400 Btu per ton of bullion. This is the quantity of heat which must be removed by the condenser coolant (in addition to the heat radiated by the bullion to the condenser).

Distillation Process

The following brief description applies not only to the distillation of zinc from lead, under a vacuum of about 10 to 100 microns, but to any similar process where the distilling element has a partial pressure of about 100 microns or greater, and the nonvolatile constituents have a partial pressure of less than about 10 microns, provided that extensive evaporating and condensing surfaces are situated parallel to one another without obstructions to vapor flow in between, and with a vapor path short enough for the resistance of the vessel walls to be neglected.

Zinc atoms leave the evaporating surface to form vapor with a partial pressure roughly half that in the distilland. The nitrogen partial pressure there is negligibly small, thus the motion of zinc vapor away from the surface is extremely rapid, and a relatively large amount of lead vapor is drawn into the stream.

Only quite close to the condensing surface does the nitrogen partial pressure rise, quite steeply, to the measured degree of vacuum. The lead content of the vapor, which is at supersaturation values, tends to lower itself by condensation to liquid globules, which are formed in an atmosphere of nearly pure zinc vapor and thus are saturated with zinc.

If the flow of vapor is vertically upward, these droplets of precondensate tend to fall back into the distilland, and the distillate will be lower in lead content, the greater the distance between evaporating and condensing surfaces.

If the vapor flow is horizontal, then the precondensate globules tend to fall toward the lower part of the condenser.

The overall rate of distillation is more dependent upon the difference in partial pressure of zinc between distilland surface and vapor just above the surface than upon any other factors. Hence a rise in evaporating temperature, which raises the vapor pressure of zinc, increases this difference, and thus markedly increases the distillation rate.

A reduction of the residual gas pressure (the vacuum) lowers the pressure of zinc vapor above the distilland surface slightly, and thus slightly improves the distillation rate. If the residual gas pressure is lowered to the point where molecular distillation can occur, a great improvement in distillation rate should result.

If the condenser temperature is high enough for the partial pressure of zinc in the distillate to be appreciable, the effect on the overall distillation rate, as compared with cold condensation, is roughly equivalent to raising the residual gas pressure by the same amount as the partial pressure of zinc in the distillate.

Alterations in the distance across the distillation space do not exert any appreciable influence on the rate of distillation, because the partial pressure of nitrogen is negligibly small over most of the space, and rises steeply only near the condensing surface.

Acknowledgments

The writer is indebted to D. R. Blaskett of the Broken Hill Associated Smelters Pty. Ltd. Research Department staff, and G. M. Willis of the Melbourne University School of Metallurgy, for many discussions which have been of great assistance in developing the concept of the distillation process which has been presented; and to K. C. Williams of the Broken Hill Associated Smelters Pty. Ltd. Research Department staff for performing the lengthy calculations of activity from Lumsden's data. The permission of the Management of Broken Hill Associated Smelters Pty. Ltd. to present this paper is also gratefully acknowledged.

References

[1] W. J. Kroll: The Vacuum Distillation of Metals. *Metal Industry* (1935) **47**, p. 155. Also, Melting and Evaporating Metals in a Vacuum. *Trans.* Electrochem. Soc. (1945) **87**, p. 571; and Vacuum Metallurgy. *Vacuum* (1951) **1**, p. 163.

[2] W. T. Isbell: Vacuum Dezincing in Lead Refining. *Trans.* AIME (1949) **182**, p. 186; METALS TECHNOLOGY (April 1947).

[3] Extractive Metallurgy in Australia. (1953) Vol. 4b. Fifth Empire Mining and Metallurgical Congress Publication.

[4] I. I. Betcherman and L. M. Pidgeon: The Distillation of Calcium and Magnesium. Canadian Min. and Met. *Bull.* (1951) **44**, pp. 253, 460.

[5] R. R. Rogers and G. E. Viens: The Refining of Magnesium by Vaporization of Extremely Low Pressures. *Journal* Electrochem. Soc. (1950) **97**, p. 419.

[6] R. R. Rogers and G. E. Viens: Refining Lithium by Vaporization at Low Pressure. Canadian Min. and Met. *Bull.* (1951) **44**, p. 15.

[7] M. J. Spendlove and H. W. St. Clair: Low Pressure Distillation of Zinc from Al-Zn Alloy. *Trans.* AIME (1949) **185**, p. 553; JOURNAL OF METALS (September 1949). Also, Rate of Evaporation of Zinc at Low Pressures. U. S. Bur. Mines Report No. 4710 (1950).

[8] W. K. Lewis and K. C. Chang: The Mechanism of Rectification. *Trans.* A.I.Ch.E. (1928) **21**, p. 127.

[9] K. K. Kelley: Contributions to the Data on Theoretical Metallurgy, Pt. III. U. S. Bur. Mines *Bull.* 383 (1935).

[10] J. Lumsden: Thermodynamics of Lead-Zinc Alloys. Discussion of Faraday Soc. (1948) No. 4, p. 60.

[11] K. Jellinek and A. Wannow: Vapor Pressures and Activities of Completely and Incompletely Miscible Metals in Liquid Binary and Ternary Alloys with One or Two Volatile Components. *Ztsch. Elektrochem.* (1935) **41**, p. 346.

[12] R. K. Waring, E. A. Anderson, R. D. Springer, and R. L. Wilcox: Equilibrium in the Lead Zinc System with Special Reference to Liquid Solubility. *Trans.* AIME (1934) **111**, p. 254.

[13] P. C. Carman: Molecular Distillation and Sublimation. *Trans.* Faraday Soc. (1948) **44**, p. 529.

[14] A. W. Schlechten: Discussion to ref. 5. *Journal* Electrochem. Soc. (1950) **98**, p. 257.

[15] H. Kramers and S. Stemerding: *Applied Scientific Research* (1951) **A3**, p. 73. Abstract in *Vacuum* (1951) **1**, p. 339.

[16] F. D. Richardson: Principles Underlying Refining Processes. P. 83. *Principles of Extraction and Refining of Metals.* (March 1951) Inst. of Metallurgists.

Technical Note

Isothermal Temper Embrittlement of SAE 3140 Steel

by F. L. Carr, M. Goldman, L. D. Jaffe, and D. C. Buffum

IN an earlier investigation by Jaffe and Buffum,[1] a time-temperature transformation diagram for isothermal temper embrittlement of an SAE 3140 steel showed some suggestion of two overlapping "noses." These authors mentioned, as a possible explanation, that their specimens embrittled at 525°C were slightly softer than expected, perhaps because of some slight unknown variation in tempering treatment. Because a double nose would be of considerable importance in elucidating the mechanism of the temper brittleness reaction,[2] it appeared worthwhile to redetermine the portion of the diagram near 525°C.

The same heat of SAE 3140 steel was used as in the previous work, and experimental procedures were the same.[1] Blanks were austenitized 1 hr at 900°C, water-quenched, tempered 1 hr at 675°C, and water-quenched. Groups were then embrittled isothermally at the temperatures and for the times shown in Table I, and water-quenched. For comparison, one series was tempered various times at 675°C, water-quenched, and given no further treatment. V-notched Charpy impact specimens machined from the blanks were tested over a range of temperatures. Energy absorption and percentage of fibrous fracture were plotted vs test temperature for each group, utilizing both the new data and those for the same treatment obtained in the earlier work,[1] except that the earlier data at 525°C were discarded.*

Table I. Transition Temperatures, °C. 100 Pct Fibrous Criterion

Embrittling Temperature, °C	Embrittling Time				
	5 Min	20 Min	1½ Hr*	8 Hr	48 Hr
450	−68	−70	−70	−69	−50
475	−70	−68	−68	−55	−20
500	−73	−74	−65	−38	+ 2
525	−65	−65	−46	−24	−18
550	−68	−63	−52	−38	−42
575	−71	−60	−59	−54	−54

Tempering Temperature, °C	Tempering Time				
	1 Hr	4 Hr	16 Hr	48 Hr	240 Hr
675	−60	−68 (Rc 21)†	−57 (Rc 19½)	−42 (Rc 15½)	−20 (Rc 10)

* This time is the average of treatments of 1 hr 20 min and 1 hr 40 min.
† Rockwell C hardness.

* One of the embrittling times used in this study was 1 hr 20 min; the corresponding time in the previous work was 1 hr 40 min. Both sets of data were plotted together. The time of "4 min" listed in the earlier paper should have read "5 min."

Hardnesses of all groups were between Rockwell C22 and C25, except where indicated in the table.

From the graphs mentioned, temperatures of transition from tough to brittle failure were read, and are given in Table I. After a small correction (−0.28°C/BHN) for the variation of hardness[3] from Rockwell C24, the transition temperatures were plotted against embrittling time for each embrittling temperature, using the data of Table I for the range of treatments covered there, and using previous data[1] for other treatments. By cross-plotting, Fig. 1 was finally obtained. It appears from this figure that if there are two noses to the time-temperature-transformation diagram for isothermal temper embrittlement of SAE 3140 steel, the upper nose must lie above 575°C.

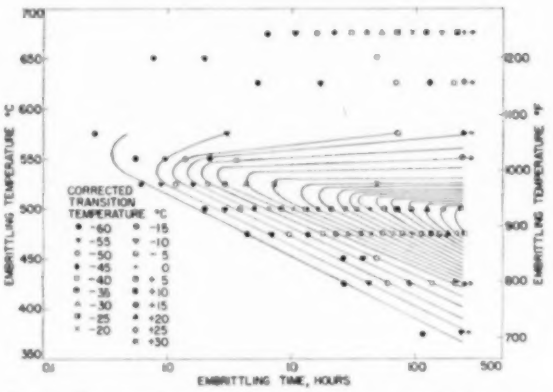

Fig. 1—Time-temperature diagram for temper embrittlement of SAE 3140 steel.

As interest had been primarily in the region near 525°C, a thorough study of embrittlement above 575°C was not made. Fig. 1 shows that such a study is needed, especially since preliminary measurements at the tempering temperature of 675°C reveal much more rapid embrittlement than would be expected from the data at lower temperatures. The transition temperature increased, approximately, as the logarithm of the tempering time (about 8½°C, after correction for hardness, for each doubling of the time).[4] Since three tensile specimens tempered 240 hr at 675°C and water-quenched had an average yield-tensile ratio of 0.844, with 70.7 pct reduction of area, it is assumed[1] that the tempering temperature is not above Ae_1. The omission of a quench-and-reheat operation below Ae_1 for the groups tempered at 675°C, as compared to groups embrittled at lower temperatures, should not affect results.[5]

More detailed investigation of embrittlement above 575°C is now under way.

References

[1] L. D. Jaffe and D. C. Buffum: Isothermal Temper Embrittlement. *Trans.* ASM (1950) **42**, pp. 604-614.
[2] M. Baeyertz: Discussion to ref. 1. *Trans.* ASM (1950) **42**, pp. 614-615.
[3] D. C. Buffum and L. D. Jaffe: Effect of Hardness on Temper Brittleness. *Trans.* AIME (1951) **191**, p. 540; JOURNAL OF METALS (July 1951).
[4] L. D. Jaffe and D. C. Buffum: Retrogression of Temper Brittleness. *Revue de Metallurgie* (1951) **48**, pp. 609-612.
[5] L. D. Jaffe, D. C. Buffum, and F. L. Carr: Effect of Various Heat Treating Cycles upon Temper Brittleness. *Trans.* ASM (1953) **45**, pp. 725-731.

F. L. CARR, associated with National Research Corp., Cambridge, Mass., and M. GOLDMAN, associated with Goodyear Aircraft Corp., Akron, Ohio, were formerly with Watertown Arsenal, and L. D. JAFFE and D. C. BUFFUM, Members AIME, are associated with Watertown Arsenal, Watertown, Mass.

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Examination of a High Sulphur Free-Machining Ingot, Bloom and Billet Sections

by D. J. Carney and E. C. Rudolphy

IT has been demonstrated that inclusion size, distribution, and composition affect the machinability of resulphurized steels. Merchant and Zlatin[1] concluded that large sulphide inclusions aided machining by forming a (lubricating) coating on the tool face. Boulger et al.[2] and Van Vlack[3] noted that the size, distribution, and composition of the inclusions in the steel affected the machinability. Steel specimens containing large globular sulphide inclusions usually exhibited excellent cutting properties, while machinability was adversely affected by the presence of numbers of oxide-type inclusions. Consequently a thorough knowledge of all the factors which affect the inclusions in the final product is desirable.

Since almost all the inclusions have their origin in liquid steel, it was necessary to begin a study of inclusions in free-machining steels by studying the inclusions and chemical segregation in the as-cast ingot. Very little information is available on the size, distribution, shape, and composition of inclusions in large, capped, free-machining steel ingots, particularly the B1113 grade. Gregory and Whiteley[4] made a general study of the inclusions in a small, high sulphur, free-machining steel ingot. Also, numerous authors have described the solidification and segregation characteristics of the four basic types of steel ingots, namely, rimmed,[5-7] capped,[7] semikilled,[7, 8] and killed[7, 8, 10] ingots. Most of these studies were made with plain carbon or low alloy, low sulphur steel.

It was desirable to study not only the ingot but also the change in size, shape, and number of inclusions on rolling an ingot to a bloom and thence to a billet. This procedure was followed and it is hoped that this study may serve the dual purpose of adding to the general knowledge of ingot solidification as well as contributing to the knowledge of the size, shape, distribution, and composition of inclusions from the ingot to the billet in a high sulphur, free-machining steel.

Procedure

A 12,000-lb 23x35x75 in. slab ingot of the B1113 grade was cast, sectioned, and studied both macroscopically and microscopically. An adjacent ingot from the same heat and of the same size was rolled to a 7⅞x7⅞ in. bloom and thence to a 2½x2½ in. billet. These various bloom and billet sections were also sectioned and studied macroscopically and microscopically.

Sectioning the Ingot: The ingot herein described was obtained from the United States Steel Corp.'s South Works Bessemer Blow No. 0193, a B1113 mechanically capped heat. The 23x35 in. ingot (No. 2) was teemed according to normal procedures and after stripping and transportation to the rolling mill was not placed in the soaking pit but allowed to air cool in an upright position. When completely solidified, the ingot was cut into sections by means of a powder scarfing torch and further sectioned by saw cutting as indicated in Fig. 1.

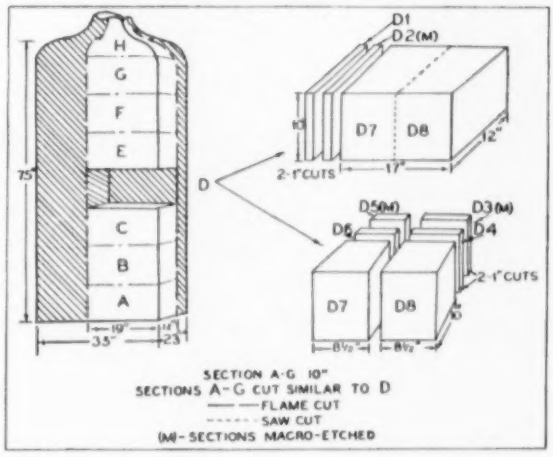

Fig. 1—Method of sectioning the B1113 ingot.

Cut No. 2 (1x10x12 in.) from sections A through H was cleaned thoroughly, macroetched in a solution of 50-50 water and hot muriatic acid and used to obtain a macrograph of a horizontal section from the surface to slightly beyond the center of the 23-in. ingot dimension. Cuts No. 5 and 3 (1x8½x10 in. each) from sections A through H were treated in a similar manner to obtain a macrograph of a horizontal section from the surface to slightly beyond the center of the 35-in. ingot dimension. The composite macrograph of these horizontal ingot sections, which shows a vertical section of the ingot from top to bottom, is shown in Fig. 2. It should be noted that sections No. 2 are normal to sections 5 and 3 in the composite.

Drillings for chemical analyses were obtained from selected positions within the above-mentioned ingot sections as noted in Fig. 3. The oxygen content was determined by the vacuum-fusion method. Samples for microscopic examination were cut from

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these, as indicated in Fig. 4. The samples were taken from the indicated positions for microscopic examination on the basis of the results of the chemical analyses. They were chosen to obtain the best relationships between chemical segregation and inclusion studies, as well as to obtain the representative microstructure and inclusion data from center to surface and from top to bottom of the ingot.

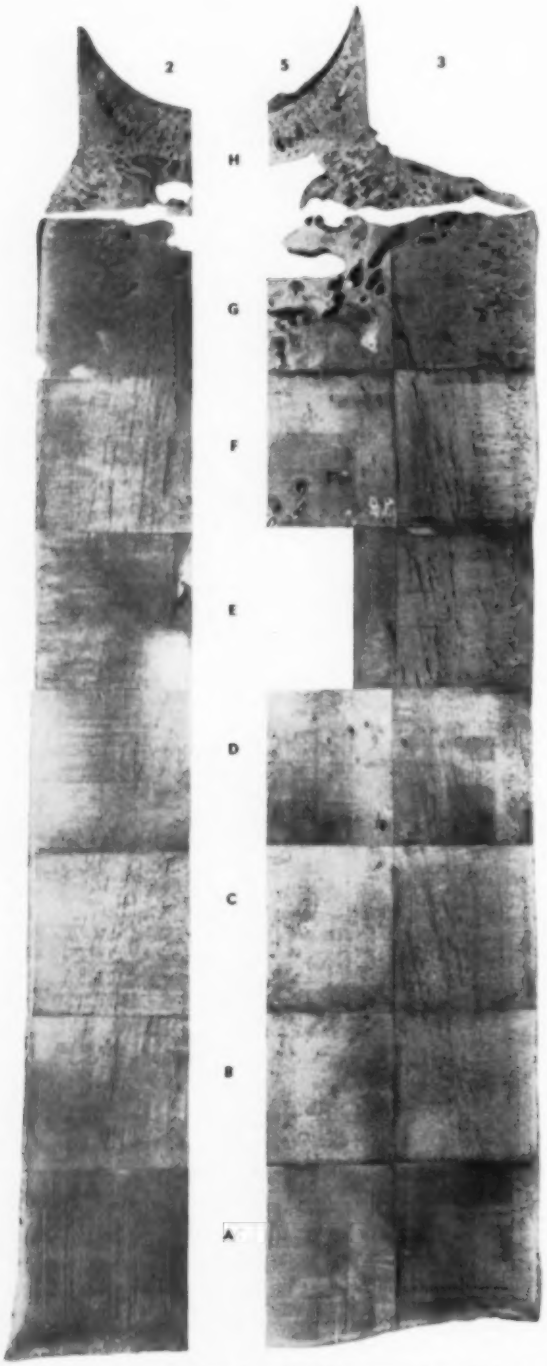


Fig. 2—Composite macrostructure of B1113 ingot. Sections 2 in a vertical plane normal to that of sections 5 and 3, see Fig. 1. 50 pct muriatic acid etch. X1/5. Area reduced approximately 75 pct for reproduction.

Sectioning of Bloom and Billet Samples: In addition to the as-cast samples obtained from ingot No. 2 samples were taken from each bloom and billet of the succeeding ingot (No. 3) of this heat. The ingot was rolled into four 7⅞x7⅞ in. x 14 ft bloom sections and thence into eighteen 2½x2½ in. x 30 ft billet sections. Cuts of 9 in. were obtained from the top of each bloom and a cut of the same size from the bottom of the bottom bloom. Cuts of 12 in. were taken from the top billet of each bloom and a 12-in. bottom cut was taken from the bottom billet of the bottom bloom. Further sectioning to sample size was done as indicated in Fig. 5.

The final bloom and billet sections were macroetched in a manner similar to the ingot sections and photographed, see Figs. 6 and 7. Samples for microscopic examination were then selected taking a full section from surface to center of each bloom and billet as shown in Fig. 5.

Microscopic Examination: All samples selected for microscopic examination were saw cut and rough finished on 0, 00, and 000 emery paper. They were then polished on a high speed polishing wheel using a polishing solution of iso-propyl alcohol and fine-grained alumina on a gammal cloth. Etching for structure and grain size was accomplished by alternate polishing and etching in a 2 pct nital solution until the proper depth of etch had been obtained.

The techniques used to measure the length-width ratios (L/W) and the number of inclusions in ingot, bloom, and billet samples were similar to those used by Van Vlack[3] and therefore will not be described in detail here. Because of the use of a different microscopic lens combination than that used in the above-mentioned work, only those inclusions greater than 0.007 mm in length were counted. However, the relative size of inclusions was calculated by utilizing the length and width values of the inclusions measured, in the equation, $V = 1.08\ LW^2$, for the determination of the relative inclusion volume (size). This method of determining relative inclusion size was developed by Van Vlack and the derivation of this equation will be found in the appendix to this text. At least 50 lengths and widths were measured at random locations within each microsection examined. The relative size of the average inclusion within the section was then calculated. For the purpose of direct comparison, the values for the size, number, and L/W ratios of the ingot inclusions were obtained from those ingot sections which would correspond with the bloom and billet samples.

Results and Discussion

Ingot—*Macroscopic Examination:* It can be noted in Fig. 2 that the capped B1113 steel ingot exhibits a structure similar to that of killed ingots rather than to that of normal low sulphur (0.04 pct maximum S) capped ingots.[4,7,9] The presence of "V" segregation, "inverted V" segregation, positive and negative chemical segregation, pipe and blowhole location tends to support this statement, see Fig. 8. Apparently the high sulphur content of the liquid metal suppressed the formation and evolution of carbon monoxide. In a previous British study[4] this same observation was made and considerable discussion of the finding was presented. It was stated that the sulphur probably deoxidized the steel. Recent work by Hilty[11] on a pure liquid iron system showed that sulphur is a poor deoxidizer. It is more reasonable to expect that sulphur suppresses the

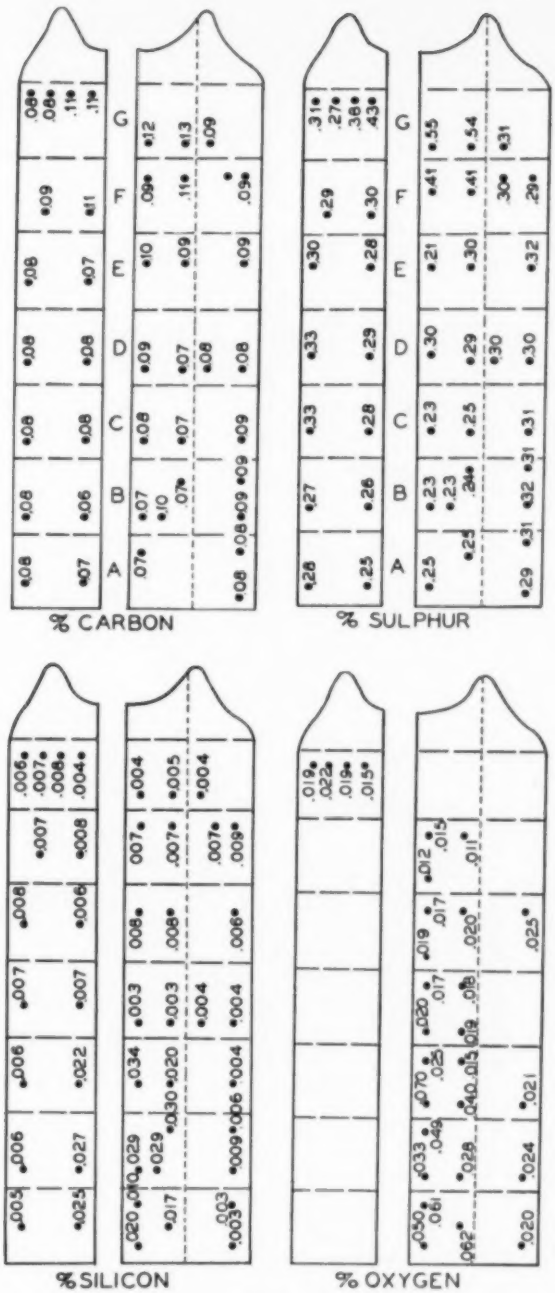


Fig. 3—Chemical analyses of samples selected from ingot sections. a, top. b, bottom.

carbon monoxide evolution by way of its affect on the chemical activity of carbon and/or oxygen.

The pipe and secondary blowholes were confined primarily to the topmost sections of the ingot, H and G. The V segregate was found in the top of section G, while the inverted-V segregate extended from section B near the bottom of the ingot to section G where it ended forming an inverted truncated cone. These features were noted also by Gregory and Whiteley in similar work with a 5000-lb ingot.[4] The V segregate was occasioned by large sulphide inclusions which were segregated in this area. Small dot etch pits that can be noted lower in the ingot in

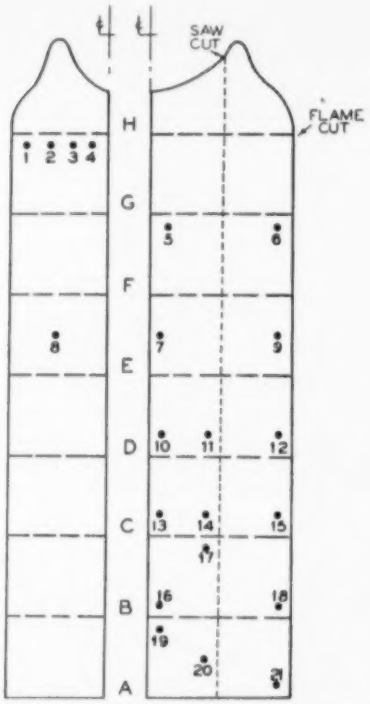


Fig. 4—Location of samples selected for microscopic examination.

sections B and C are caused by silicate inclusions. These observations are confirmed by examination of microsections and chemical analyses, see Fig. 9 and Table I.

The rate of solidification of the ingot from the bottom was rapid. Furthermore, no patches of sulphide or dot etch were evident in this section (A), so that the extreme bottom portion of the ingot was sound steel. At the surface of the bottom section where inclusions were noted in number, they were exceptionally fine, further evidence of rapid solidification along the mold wall.

Chemical Segregation: Chemical analyses are summarized in Table I and Fig. 3. Maximum positive chemical segregation was confined to the topmost sections of the ingot, G and F, in the case of carbon, sulphur, phosphorus, and manganese. Silicon and oxygen tended to segregate positively in the bottom third of the ingot in which the above-mentioned elements tended to reach maximum negative segregation.

Sulphur tended to segregate positively in the center of the top one third of the ingot while silicon

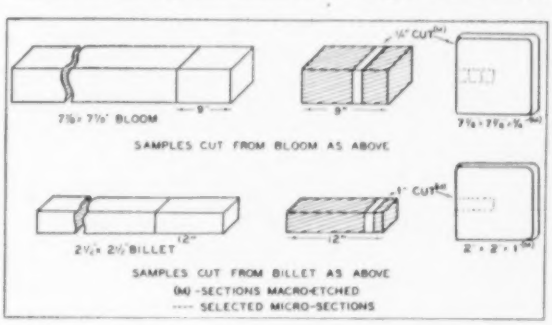
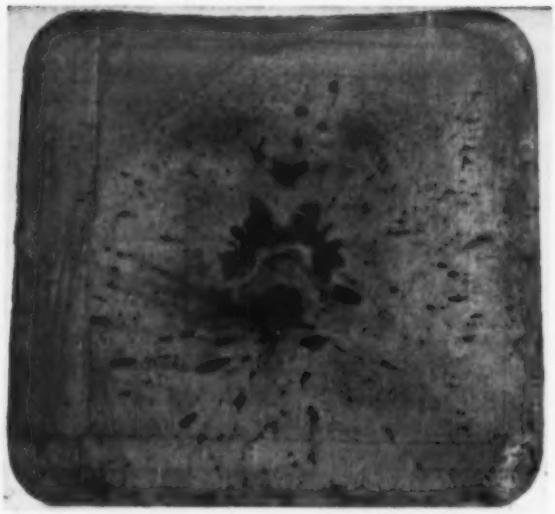
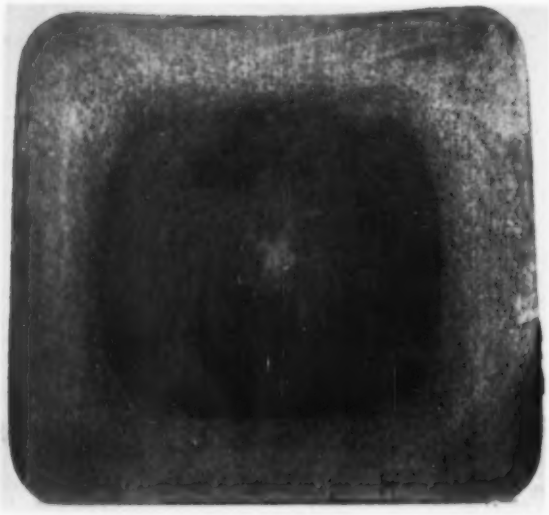


Fig. 5—Method of sectioning the bloom and billet samples.

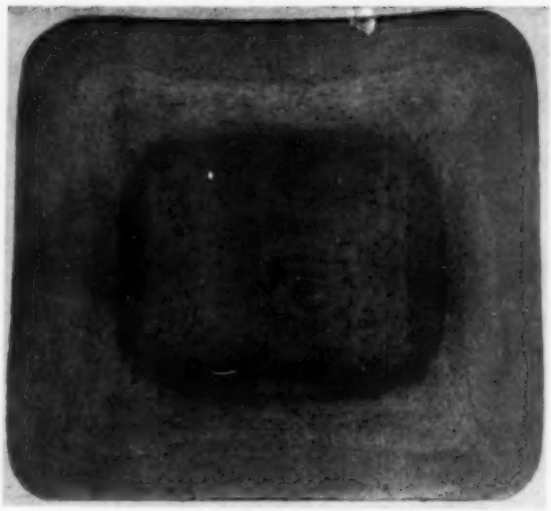


a—Bloom 1—top.

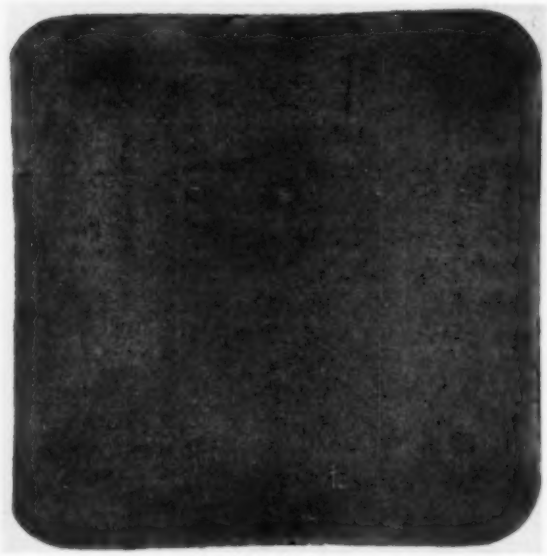


b—Bloom 2—top.

c—Bloom 3—top.



d—Bloom 4—top.



e—Bloom 4—bottom.

Fig. 6 a to e—Macrostructure of B1113 bloom sections. Locations given in Fig. 5. 50 pct muriatic acid etch. Area reduced approximately 75 pct for reproduction.

and oxygen showed positive segregation toward the center of the bottom of the ingot. Lower oxygen levels were observed in those sections with the higher sulphur content. The segregation of carbon, manganese, phosphorus, and nitrogen was very similar to that noted in capped ingots with lower sulphur contents. However, this segregation was not considered to be of any real significance in this study.

The presence of higher oxygen contents in the bottom cuts of ingots was suspected in earlier work and confirmed by oxygen analyses of B1112 and B1113 bar samples which had shown poor machining qualities.[5] A similar segregation of oxygen has been noted in the examination of an ingot with approximately the same composition.[4] Although the segregation of silicon and oxygen in the bottom of the ingot has never been explained satisfactorily, it was observed microscopically that the presence of high oxygen in these sections of the ingot is the re-

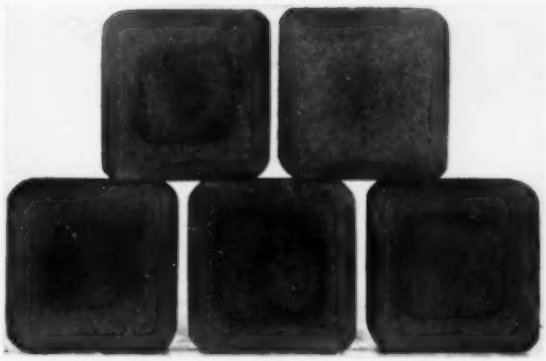


Fig. 7—Macrostructure of B1113 billet sections. Locations given in Fig. 5. 50 pct muriatic acid etch. Upper row: left, 15T; right, 18B. Lower row: left, 2T; center, 6T; right, 10T. Area reduced approximately 75 pct for reproduction.

sult of siliceous inclusions, Fig. 9. The analytical methods used in this report for analyses of steel for silicon and oxygen yield the total silicon and total oxygen contents, with no distinction as to the quantity of oxygen or silicon dissolved in the metal or in the inclusions. The explanation of the segregation of silicon and oxygen as silica in the bottom of the ingot and sulphur in the top of the ingot probably lies within the phase relationships of the liquidus surface of the Fe-Si-Mn-S-O system. Recent data on the Fe-S-O system[11] indicate the presence of two immiscible liquids. Possibly the segregation of silica and sulphur during the solidification of the ingot is related to immiscible silica and sulphide phases.

Microscopic Examination: Most of the inclusions in the ingot tended to be globular in shape regardless of location or apparent composition. This is shown by the proximity to unity of the length-width ratios (L/W), Table I and Fig. 9. Also, the inclusions tended to decrease in size but to increase in number from the center to the surface of the ingot. This was true in all sections from the top to the bottom of the ingot as shown in Fig. 10.

The predominant type of inclusions noted varied considerably, depending on ingot position, and this variation is shown pictorially in Fig. 9. In the top part of the ingot large single-phased MnS inclusions were most common, but numerous duplex (Fe,Mn) sulphides were found in sections G and F.[12] Several FeS inclusions, which as such are relatively uncommon in commercial steels, were also noted in sections G and F,* see Fig. 11. Occasional oxide-sulphide duplex inclusions were noted at the bottom of section E, as the study progressed from the top toward the bottom of the ingot. The constituents of these duplex inclusions are usually MnS and a glassy phase which is $MnO \cdot SiO_2$ glass,† although some FeO has been noted.

* MnS will dissolve up to about 50 pct FeS in solid solution. The exact amount is dependent upon the manganese and sulphur content of the steel. Likewise the sulphide phase will dissolve an undetermined amount of oxygen.

† The etching characteristics indicate that the siliceous glass is comparatively rich in MnO.

In section C from the center to midway to the surface, the majority of the inclusions were large and siliceous in type, although there were numbers of these inclusions containing small globules of manganese sulphide. In sections A, B, and C, where chemical analyses revealed high silicon and oxygen, these siliceous inclusions were found, as well as the negative segregation of sulphur. The negative sulphur segregation was evidenced by fewer sulphide inclusions in the center of the ingot in sections A, B, and C than noted in the upper sections of the ingot. Sulphide inclusions were most prevalent in these sections from the center to the surface but the siliceous type of inclusion was more prominent from the ingot center to midway to the surface. In the ingot sections that were low in oxygen content the inclusions were primarily single-phase sulphide inclusions, whereas in sections that were high in oxygen the inclusions were of the duplex or single-phase siliceous type. It should again be mentioned that an earlier investigation[8] showed that bottom cut bar samples showed poor machining properties which were attributed to these glassy oxide inclusions. Armour[13] also observed that the presence of glassy oxide inclusions had an adverse effect on machinability by causing a reduction in tool life.

The explanation of the duplex nature of some of the inclusions is probably closely related to the aforementioned explanation of silica segregation. It is plausible that within this system the sulphide and silicate phases separate as a pair of liquids, and the manganese silicate may then devitrify from a glass.

The general crystal structure of the ingot from center to surface as determined by examination of the etched microsections is shown in Fig. 12. As can be seen in this figure, the chill zone consists of fine equiaxed grains of ferrite. Inside this surface zone, which was very thin, was a section of columnar dendritic ferrite crystals, almost normal to the ingot surface. Midway to the center of the ingot, the core of larger equiaxed ferrite grains was noted.

The process of solidification caused the entrapment of less pure liquid between the crystals in the columnar zone as indicated by pearlite in the grain boundaries. The slight segregation of carbon in the top center portion of the ingot was also indicated by an increased amount of pearlite, Fig. 12.

In general, the inclusions (regardless of composition) were found within the ferrite grains. In the midway position at the top of the ingot the iron sulphide inclusions and some manganese sulphide inclusions were observed at the ferrite grain boundaries.

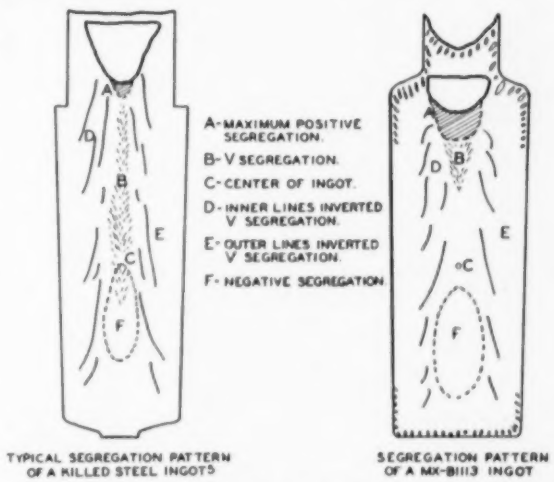


Fig. 8—Schematic comparison of killed ingot structure with B1113 ingot.

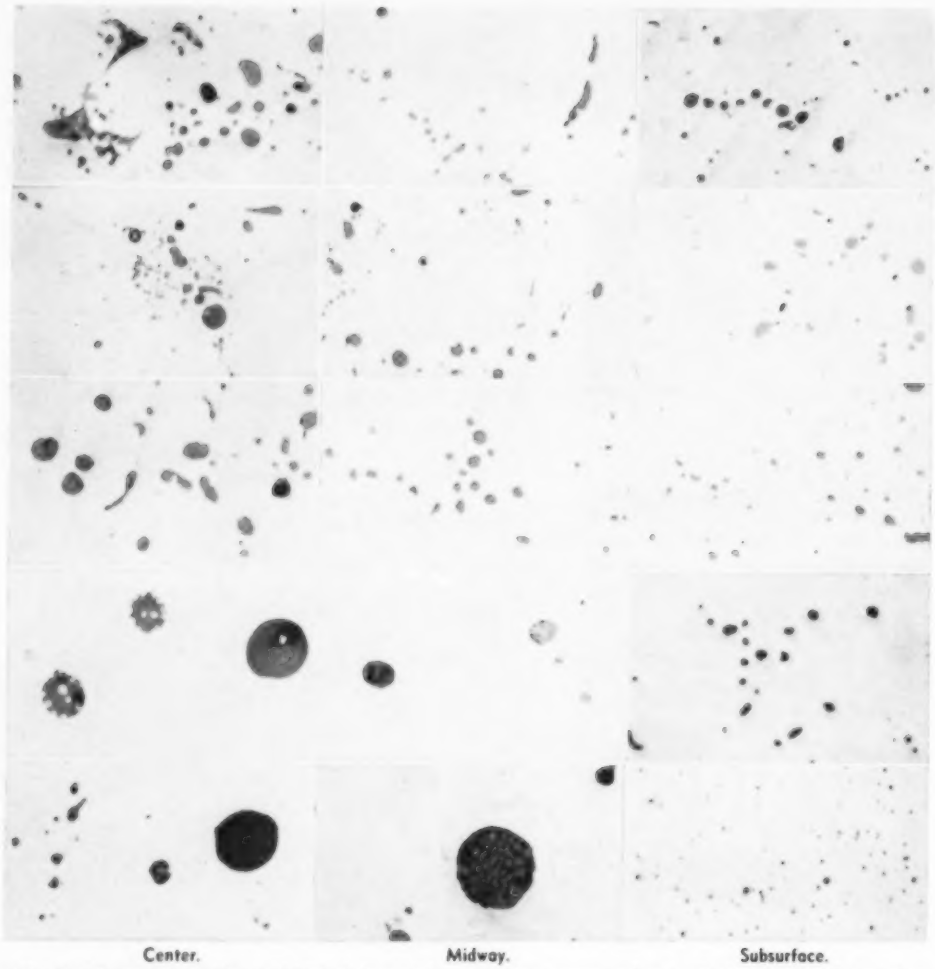


Fig. 9—Micrographs showing typical inclusions at ingot positions corresponding to the bloom and billet sections. Unetched. X100. Area reduced slightly for reproduction.

Bloom—The chemical analyses of the bloom sections are summarized in Table II and the macrographs of the etched bloom sections are shown in Fig. 6.

Chemical and Macroscopic Examination: In examining the macroetched topmost section of the bloom samples, a large blotchy area was noted in the central portion of this sample, Fig. 6a. Chemical analyses in this area in the bloom sample indicated a high sulphur content. Chemical analyses of ingot samples from the corresponding section, which was

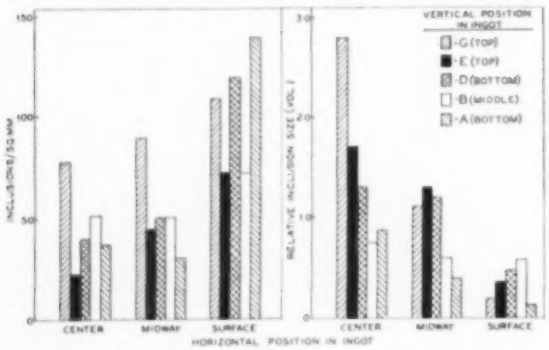


Fig. 10—Number and relative size of inclusions at ingot positions corresponding to the bloom and billet sections.

very porous and contained large blowholes, showed approximately the same sulphur content. These blowhole cavities were closed on rolling and the larger ones appeared to have been filled with the lower melting, sulphur-rich metal in the top of the ingot. This can be further indicated by the sharp boundaries in this area of the top bloom section, Fig. 6a.

The double etch pattern, as shown in Fig. 6c and b, appeared to result from sulphide inclusions in the outer pattern and silicate inclusions in the inner pattern. It has been mentioned in the literature[14] that this pattern effect is due to crystallization of the ingot, and is found in the part of the rolled product that was the columnar structure of the ingot. There was no evidence in this work that showed the concentration of either type of inclusion in a given crystal structure, although there were more sulphides noted toward the surface.

Microscopic Examination: Micrographs of typical bloom sections are shown in Figs. 13 and 15. The inclusion study data on the bloom sections are summarized in Table II and shown graphically in Figs. 14 and 16.

In rolling the ingot to 7⅞x7⅞ in. blooms, the *L/W* ratio of the inclusions was increased as much as five times. This resulted in longer, thinner inclusions as compared to the essentially globular in-

Table I. Chemical Composition and Inclusion Study Data of B1113 Ingot Heat No. 0193, Ingot No. 2

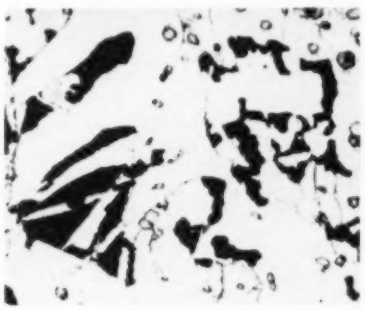
Ladle Analysis: C, 0.08 pct; Mn, 0.88; P, 0.11; S, 0.30; and Si, 0.007. Poured at 2885°F. Rolled at 2375°F.

Ingot Section	Position*	Chemical Composition, Pct							Average Inclusions per Sq Mm	Average L/W	Average Relative Inclusion Size
		C	Mn	P	S	Si	O	N			
G2	c	0.11			0.43	0.004	0.015	0.009	103	1.0	
	m_1	0.11		0.16	0.38	0.008	0.019	0.007	77	1.4	1.30
	m_2	0.08			0.27	0.007	0.022	0.008	111	1.2	
	s	0.08	0.94	0.12	0.31	0.006	0.019	0.009	77	1.2	
G5 and 3	c	0.12		0.10	0.55	0.004					
	m_1	0.13			0.54	0.005					
	m_2	0.09			0.31	0.004					
F2	c	0.11			0.30	0.008					
	s	0.09			0.29	0.007					
F5 and 3	c	0.09	0.95	0.16	0.41	0.007	0.015	0.012	32	1.4	
	m_1	0.11	0.96	0.15	0.41	0.007	0.011	0.015			
	m_2	0.09	0.92	0.12	0.30	0.007					
	s	0.08	0.95	0.11	0.29	0.009			103	1.3	
E2	c	0.07	0.92	0.12	0.28	0.006			49	1.4	
	s	0.08			0.30	0.008					
E5 and 3	c	0.10			0.21	0.008	0.017	0.010	22	1.3	
	m	0.09			0.30	0.008	0.020	0.017			0.72
	s	0.09			0.32	0.006	0.025	0.010	74	1.3	
D2	c	0.08			0.29	0.007					
	s	0.08			0.31	0.007					
D5 and 3	c	0.09	0.87	0.11	0.30	0.003	0.020	0.010	40	1.1	
	m_1	0.07	0.86	0.12	0.29	0.003	0.019	0.005	52	1.4	0.97
	m_2	0.06			0.30	0.004					
	s	0.08	0.91	0.12	0.30	0.004			123	1.3	
C2	c	0.08			0.28	0.022					
	s	0.09			0.33	0.006					
C5 and 3	c	0.08			0.23	0.034	0.070	0.008	62	1.3	
	m	0.07			0.25	0.020	0.040	0.006	57	1.2	
	s	0.09			0.31	0.004	0.021	0.012	92	1.1	
B2	c	0.06			0.26	0.027					
	s	0.08	0.87		0.27	0.006					
B5 and 3	c_1	0.07			0.23	0.029	0.033	0.010	57	1.0	
	c_2	0.10	0.86	0.087	0.23	0.029	0.028	0.011			0.64
	m	0.07	0.95		0.24	0.030			52	1.1	
	s	0.09			0.32	0.009	0.024	0.011	72	1.2	
A2	c	0.07			0.25	0.025					
	s	0.08			0.28	0.005					
A5 and 3	c (top)	0.07				0.020	0.061	0.007	37	1.2	
	c (bot.)				0.25	0.010	0.050	0.007			
	m				0.25	0.017	0.062	0.009	33	1.1	0.47
	s (top)	0.08			0.31	0.003					
	s (bot.)	0.08			0.29	0.003	0.020	0.006	150	1.2	

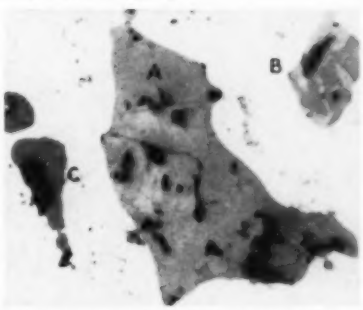
* c, center; m, midway; s, surface.

got inclusions. This increase in L/W ratio is indicated in Fig. 13A, and is shown graphically in Fig. 16. The inclusions in the samples from blooms 1T and 2T tended to retain their globular shape, but as shown in Fig. 13A the inclusions in bloom samples 3T and 4T have rolled out into stringer-type inclusions. It was in the corresponding ingot locations that siliceous inclusions segregated and examination of these bloom inclusions showed that most of these long stringers were of the siliceous inclusion type although some sulphide inclusions had also rolled out. In the 4B bloom sample, inclusions of both types were found, the sulphides tending to retain their globularity, and the silicates being strung out. This indicates that the inclusion composition had an important effect on inclusion plasticity.

In addition to the changes in L/W ratio, there was



a (left)—Carbon segregation in section G. 2 pct nital etch. X100.



b (right)—Large FeS and (Fe, Mn)S inclusions in ingot sections F and G. A, FeS. B, (Fe, Mn)S. C, MnS. Unetched. X400.

Fig. 11—Micrographs showing some effects of chemical segregation in the top sections of the B1113 ingot.

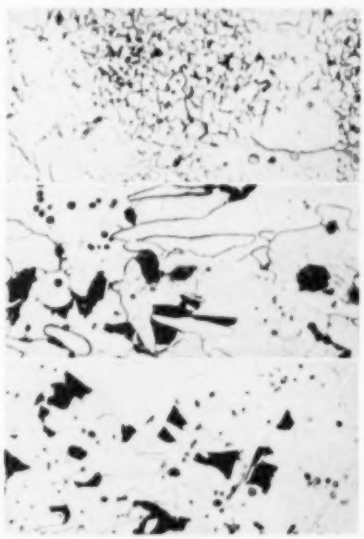


Fig. 12—Micrographs showing variation in microstructure from center to surface of ingot section D. Similar variations were noted at other levels. 2 pct nital etch. X100. Area reduced approximately 75 pct for reproduction.

Table II. Chemical Composition of B1113 Bloom Sections. Heat No. 0193, Ingot No. 3

Bloom	Position	C	Mn	P	S	Si	Average Inclusions per Sq Mm	Average L/W	Average Relative Inclusion Size
3-1-T	c-seg(A)				0.42	0.003	119	2.0	0.28
3-1-T	c-seg(B)				0.61	0.003			
3-2-T	c	0.08	0.92	0.12	0.30				
	m_1	0.10			0.37	0.004	95	3.2	0.36
	m_2	0.08			0.37	0.005			
	s	0.09			0.32	0.005			
3-3-T	c(A)				0.27	0.008			
	c(B)				0.27	0.004	95	5.6	0.35
	s(A)				0.30	0.006			
	s(B)				0.32	0.004			
3-4-T	c	0.07	0.92	0.10	0.25	0.006			
	m_1				0.25	0.020	112	5.0	0.39
	m_2	0.08			0.25	0.005			
	s(A)	0.09			0.30	0.006			
	s(B)				0.32	0.008			
3-4-B	c				0.25	0.011			
	m				0.27	0.010	119	2.3	0.36
	s				0.29	0.006			

an increase in the number of inclusions and a decrease in relative inclusion size, in rolling from ingot to bloom. Although the number of inclusions did increase, there was no major fracturing of the inclusions. The decrease in the relative size of the inclusions can be related to this increase in number, which in turn can be related to mechanical deformation and inclusion composition. This has been noted in previous work,[2,3] that the number, size, and shape of the inclusions are influenced by the plasticity of the inclusion which is affected by the composition and mechanical working.

The structural changes that took place during rolling from the ingot to bloom stage are shown in Figs. 12 and 15. The ferrite grain size of the ingot was predominantly No. 1 and larger.‡ The grain size was reduced to No. 3 to No. 4 in the blooms.

‡ ASTM austenite grain size ratings at 100X.

Billets—*Macroscopic Examination:* A macrograph

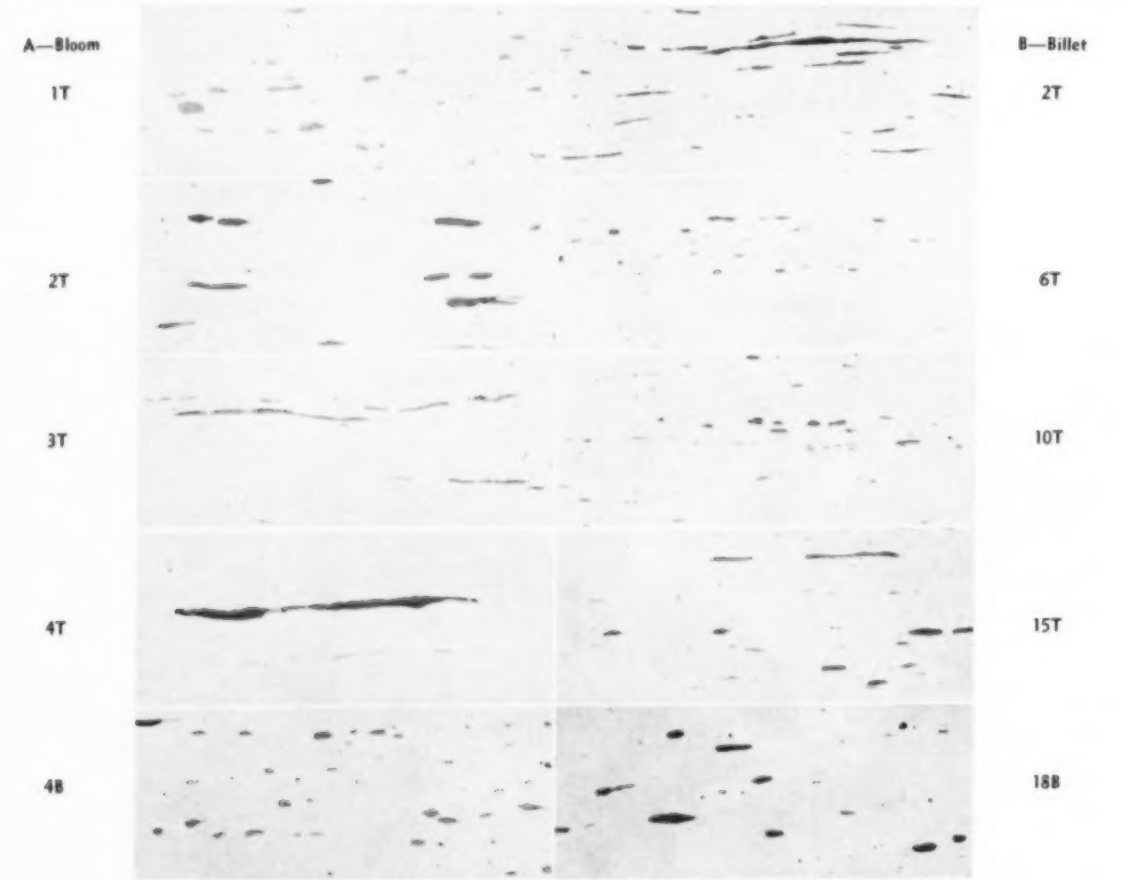


Fig. 13—Micrographs showing typical inclusions at corresponding positions in B1113 bloom and billets. These positions are also related to those in Fig. 9. Unetched. X100. Area reduced approximately 30 pct for reproduction.

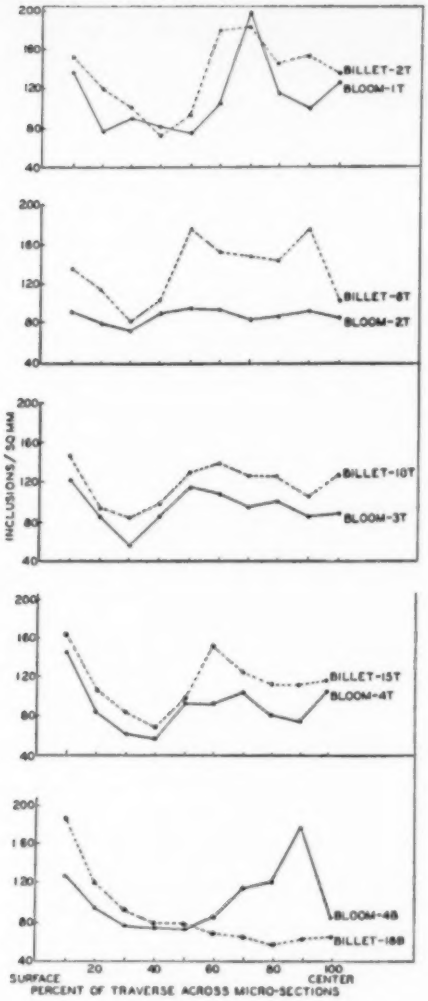


Fig. 14 (left)—Relationship between number of inclusions and percentage of traverse from surface to center of the same B1113 bloom and billet sections shown in Fig. 13.

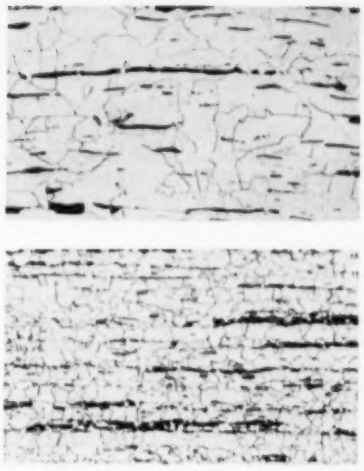


Fig. 15 (upper right)—Micrographs showing typical microstructure of B1113 blooms and billets reduced from adjacent portion of the same bloom. Bloom reduced from same section of ingot shown in Fig. 12. 2 pct nital etch. X100. Area reduced approximately 75 pct for reproduction. Upper micrograph—Bloom 3T. Lower micrograph—Billet 10T.

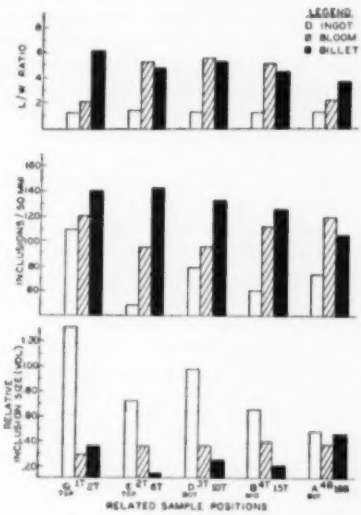


Fig. 16 (lower right)—Ingot to bloom to billet inclusion relationships.

of the etched billet sections is shown in Fig. 7. Examination of these sections indicated structures similar to those noted in the larger bloom sections. In the top billet of the top bloom the same blotchy high sulphur area as noted in the top bloom (Fig. 6a) was present. The double ingot pattern noted in blooms 3T and 4T was again present in the corresponding billet sections, 10T and 15T.

Microscopic Examination: Micrographs of typical billet sections are shown in Figs. 13 and 15 and the related inclusion studies are summarized in Table III and shown graphically in Figs. 14 and 16.

Further rolling from the 7⅞x7⅞ in. bloom size to 2½x2½ in. billets produced the following changes in inclusion size, shape, and distribution. The number of inclusions increased approximately 20 pct on rolling from bloom to billet. There was some fracturing of inclusions but still not to any major extent. The inclusions in billets 2T, 6T, and 16T appear to have been rolled out and pinched off to a

Table III. Inclusion Study Data of B1113 Blooms and Billets

Bloom No.	Inclusions per Sq Mm										Billet No.
	(Surface)			Pct of Micro Traverse						(Center)	
	10	20	30	40	50	60	70	80	90	100	
I	160	74	91	83	77	100	203	115	100	138	
	150	118	83	71	123	178	180	141	127	133	2
II	96	87	78	102	98	93	86	90	93	81	
	135	111	85	105	178	153	151	141	183	110	6
III	123	87	63	84	116	108	93	96	83	87	
	143	95	83	101	133	140	125	125	110	122	10
IVT	143	80	60	59	93	91	109	82	77	145	
	170	105	80	68	103	153	141	115	113	118	15
IVB	130	93	75	73	97	100	130	120	187	90	
	183	83	92	78	73	66	65	60	58	63	18

degree, while those in billet 15T have been strung out and in the case of the siliceous-type inclusions some have been fractured. In Fig. 14 the relationship of the number of inclusions in the bloom to the number in the billets is shown graphically. In reference to bloom 4B and billet 18B there appears to be a relationship that does not occur in the top four blooms and billets. This is caused by the method of inclusion counting, as there is a minimum size (0.007 mm) to the inclusions counted as described earlier in the text.

The inclusion size decreased and the length-width ratio remained approximately the same or increased slightly. The changes in length-width ratio and inclusion size as well as the number again appear to have been affected by inclusion composition and mechanical deformation. The greatest number of inclusions are found at the surface in all the rolled sections. This can be explained by the fact that the inclusions near the surface of the ingot are smaller and in rolling this portion probably undergoes the greatest mechanical deformation. Further structural changes that took place during rolling from the bloom stage are shown in Fig. 15. The ferrite grain size reduced to No. 3 to No. 4 in the blooms, was further reduced to No. 6 to No. 8 in the billets. It is recognized that the grain size is dependent upon finishing temperature and the cooling rates associated with the different section sizes.

Conclusions

Ingot—1—The mechanically capped, high sulphur B1113 ingot solidified in a manner similar to that of a killed-steel ingot with very little apparent gas evolution.

2—The segregation of carbon, manganese, phosphorous, and nitrogen was similar to that noted in capped ingots with low sulphur contents.

3—Silicon and oxygen segregated positively in the center of the bottom one third of the ingot, while sulphur segregated positively in the center of the top of the ingot. This was the result of the segregation of silicate and sulphide inclusion phases.

4—The ingot inclusions tended to be globular regardless of composition.

5—The rate of solidification in from the bottom was so rapid that the extreme bottom section had relatively few inclusions of any size.

6—Inclusion size increased while the number of inclusions decreased moving from the surface to the center of the ingot.

Blooms and Billets—1—The length-width ratio (L/W) of the inclusions increased approximately four-fold on rolling the ingot to blooms.

2—In rolling from ingot to billet the inclusion size decreased approximately 60 pct.

3—The composition of the inclusion had the greatest effect on the reaction of the inclusions to mechanical deformation, with the more plastic siliceous inclusions having been elongated on rolling from the ingot to blooms and billets. The sulphide inclusions tended to retain a more globular shape.

4—Blowhole cavities in the top of the ingot, which were closed on rolling, were surrounded by a low melting, sulphur-rich metal, and the larger cavities appeared to have been filled with this low melting metal on rolling.

5—The ferrite grain size of the ingot was No. 1 and larger, and was reduced to No. 3 to No. 4 in the blooms and No. 6 to No. 8 in the billets.

Acknowledgments

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Appendix-Volume of Inclusions

Assume an inclusion in rolled steel has the shape of a prolate spheroid, with the following dimension: length, $2a$; width, $2b$; volume, $4/3\ \pi ab^2$. The average length L, and average width, W, of all planes through the spheroid, parallel to a and b respectively are:

$$L = \frac{\frac{\pi ab}{dy}}{\frac{2b}{dy}} \qquad W = \frac{\frac{\pi b^2}{dz}}{\frac{2b}{dz}}$$

$$L = \frac{\pi}{2}a \qquad W = \frac{\pi}{2}b$$

$$a = \frac{2}{\pi}L \qquad b = \frac{2}{\pi}W$$

Therefore, the volume of the average spheroid is

$$V = \frac{4}{3}\pi\left(\frac{2}{\pi}L\right)\left(\frac{2}{\pi}W\right)^2$$

$$V = 1.08\,LW^2$$

A statistical error in this calculation is enlarged by the W^2.

References

[1] M. E. Merchant and N. Zlatin: Basic Reasons for Good Machinability of "Free Machining" Steels. *Trans.* ASM (1949) **41**, pp. 647-672.

[2] F. W. Boulger, H. A. Moorhead, and T. M. Garvey: Superior Machinability of MX Explained. *Iron Age* (May 17, 1951) **167**, pp. 90-95.

[3] L. H. Van Vlack: Correlation of Machinability with Inclusion Characteristics in Resulphurized Bessemer Steels. ASM Preprint No. 16, 1952; Presented at the 34th Annual ASM Convention, Philadelphia (October 20-24, 1952).

[4] E. Gregory and J. H. Whitely: Examination of a High-Sulphur, Free Cutting Steel Ingot. *Journal* Iron and Steel Inst. (1941) **144**, No. 2, pp. 9-32.

[5] A. Hayes and J. Chipman: Mechanism of Solidification and Segregation in a Low Carbon Rimming Steel Ingot. *Trans.* AIME (1939) **135**, pp. 85-125.

[6] A. Hultgren and G. Phragmen: Solidification of Rimming Steel Ingots. *Trans.* AIME (1939) **135**, p. 133.

[7] B. R. Queneau: The Solidification of Steel Ingots. *The Solidification of Metals and Alloys* (1951) pp. 52-73. AIME.

[8] M. Tenenbaum: Structure, Segregation and Solidification of Semi-Killed Steel Ingots. *Trans.* AIME (1948) **176**, pp. 108-162; METALS TECHNOLOGY (September 1947).

[9] J. W. Spretnak: Macro-Segregation in Some Alloy Steel Ingots. *Trans.* ASM (1948) **40**, pp. 897-916.

[10] B. M. Larsen: Review of Factors Underlying Segregation in Steel Ingots. *Trans.* AIME (1945) **162**, p. 414.

[11] D. C. Hilty and W. Crafts: The Liquidus Surface of the Iron-Sulphur-Oxygen System. Unpublished—private communication.

[12] C. E. Sims: Non-Metallic Inclusions. *Basic Open Hearth Steel Making.* (1944) p. 293. AIME.

[13] J. D. Armour: Metallurgy and Machinability. *Machining-Theory and Practice* (1950) p. 142. ASM.

[14] Macro-Etching of Iron and Steel. (1948) p. 393. Sub-Committee on Macro-Etching. *Metals Handbook.* ASM.

Reducing Period in Stainless Steel Melting

by H. P. Rassbach and E. R. Saunders

MUCH progress has been made in recent years in the theory and practice of making stainless steel. By effective utilization of oxygen for decarburization and more suitable alloying agents, it has been possible to attain consistent production of very low-carbon stainless steel. In order to facilitate economical production of stainless steels, the Electro Metallurgical Co. has carried out an extended experimental program that has clarified some of the complex interrelations of temperature and composition under decarburizing and reducing conditions. These results[1-3] have been founded in large part on small experimental heats, and in order to confirm their validity and significance under commercial conditions, a survey of stainless steel melting practice has been made with the cooperation of stainless steel producers.

Conditions required for decarburization and associated oxidation of chromium, manganese, and iron have been fairly well established in relation to the beneficial effect of the highest practicable temperature. The recovery of chromium and manganese from highly oxidized slags by reduction with silicon has been indicated with somewhat less precision and this study has shown significant deviation in large commercial heats from the small experimental heats. In spite of an unsatisfactory degree of accuracy in estimating the conditions affecting reduction of metallic values, it has been possible to calculate a slag weight in reasonably good agreement with the results observed in large heats. While there still is much to be learned about both the qualitative and quantitative aspects of stainless steel melting, this survey has indicated the manner by which the efficiency of the production process may be measured.

Oxidation Period

In order to establish practices for the recovery of chromium and manganese from the slag the amounts of these metals oxidized should be known. Moreover, since reduction of oxidized chromium and manganese must necessarily be accompanied by similar reduction of iron, knowledge of the total quantity of metallics oxidized is essential.

The relations between carbon, chromium, and temperature under oxidizing conditions were developed by Hilty in 1948.[1] While it had been realized previously that retention of chromium in the metal during carbon oxidation is favored by high temperatures, the Hilty relation provided quantitative information useful for evaluating melting procedures. For example, it was shown that decarburization to moderate carbon levels can be achieved while retaining substantial amounts of chromium. However, in decarburizing to the low-carbon level necessary for producing 0.03 pct maximum carbon stainless steel, very little chromium remains in the bath at the temperatures generally employed. For this reason, Hilty, Healy, and Crafts[2] later projected an extension of the chromium-carbon relation to the low-chromium region.

Although this chromium-carbon-temperature relation defined the composition of a chromium steel bath at the end of the oxidizing period, it did not provide a direct means for estimating the total amount of metallic oxidation occurring during decarburization of a stainless steel heat. This subject was investigated by Crafts and Rassbach[3] and, later, by Hilty, Healy, and Crafts[2] who demonstrated that metallic oxidation is a function of the chromium content of the initial furnace charge, the minimum carbon content attained, and the temperature. It was further demonstrated from data on 1-ton heats that an empirical relationship exists between the ratio of chromium plus manganese to iron in the slag (S) to the corresponding ratio of these components present in the metal bath. The following expression was derived to permit the calculation of the amount of metallics oxidized during decarburization of a given charge:

$$W = 2000\,\frac{(Cr_1 + Mn_1) - (Cr_2 + Mn_2)}{\frac{100S}{S+1} - (Cr_2 + Mn_2)} \qquad [1]$$

where W is the pounds of chromium, manganese, and iron oxidized per ton of charge; Cr_1, the percentage of chromium in the charge; Mn_1, the percentage of manganese in the charge; Cr_2, the percentage of chromium in the bath after oxidation; Mn_2, the percentage of manganese in the bath after oxidation; and $S = \frac{\%\ Cr + \%\ Mn}{\%\ Fe}$ in the slag after oxidation.

In order to establish whether the slag ratios of commercial heats are consistent with those found in the experimental heats, the slag and metal analyses shown in Table I were evaluated. These data represent samples taken after the oxidation of two 1-ton and seven 15 to 25-ton heats of types 303, 304, and 304L stainless steel made in chromite, acid, and basic hearths.

Fig. 1 illustrates that the results for the commercial heats correlate reasonably well with the relationship originally established for experimental 1-ton heats. It will be noted that in the range of metal composition of these heats, the slag values generally lie above the line. As was suggested by

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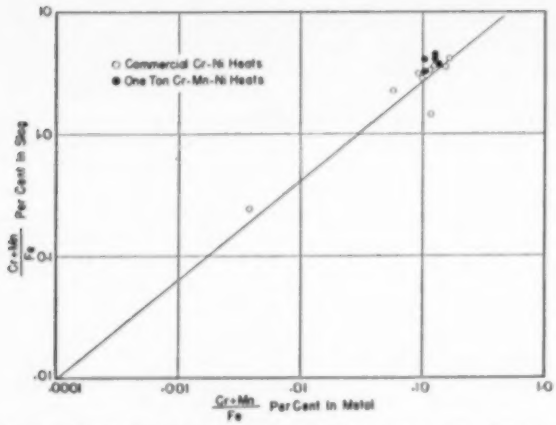

Fig. 1—Correlation of ratios of Cr+Mn/Fe in slag with relationship proposed by Hilty, Healy, and Crafts.[2]

Hilty, Healy, and Crafts the relationship may be better defined by two intersecting lines, but sufficient information is not available to justify such a representation. In view of the agreement shown, it is concluded that an estimated value of the slag may be used for the calculation of metallics oxidized in commercial heats.

This relation may also be expressed in terms of the total metallics oxidized. By use of Eq. 1, the total amount of metallics oxidized was calculated using both the actual S and the estimated S values for the commercial chromium-nickel heats, Fig. 2.

In order to determine the utility of this relationship for wider ranges of composition, data from five experimental 1-ton heats of high-manganese, chromium-nickel steels have been included in Figs. 1 and 2. These results also correlate reasonably well with the original curve indicating that manganese appears to be equivalent to chromium in this relationship.

Through the use of Fig. 1 for estimating S in Eq. 1 and by employing the published chromium-carbon-temperature relations for estimating the composition of the bath after oxidation, the amount of metallic oxidation occurring in heats oxidized to any given carbon level at any specified temperature can be predicted for charges containing various amounts of chromium, manganese, and nickel. On this basis, Fig. 3 has been prepared for a representative range of carbon contents and temperatures and an arbitrary assumption of 10 pct Ni in the bath after oxidation.

The metallics oxidized for the commercial chromium-nickel and experimental high-manganese, chromium-nickel heats, calculated on the basis of the actual slag analyses, are shown on these charts using temperatures estimated from the chromium-carbon relation. Assuming that the temperature at the end of oxidation is known from past performance or can be estimated from chromium and carbon analyses, the charts provide a reasonably accurate basis for estimating the total amount of chromium, manganese, and iron oxidized—the information necessary for establishing a reduction practice.

Slag Reduction Period–Review

It has long been known that the recovery of chromium in stainless steel melting is related to some extent to the refractory hearth employed, that is, the basic, chromite, and acid hearth process. In commercial experience better recovery of chromium is realized with the basic process than with the other processes, and the difficulties encountered in attempts to recover chromium from the slag in acid and chromite hearth heats have been described.[4,5] A common feature of the acid and chromite hearth processes is that refractory erosion is less severe when acid or neutral slags are employed. It has been generally realized that basicity is a major factor controlling the chromium content of slags, but quantitative data have become available only recently.

In the reducing period, after completion of oxidation and for the purpose of recovering metal from the slag, it has been the practice to add silicon or aluminum or both. Silicon is the element most widely used for slag reduction, and the commonly used alloys are low in carbon and contain chromium and silicon in varying concentration. Under the conditions of the reducing period the reaction of silicon with the metallic oxides in the slag is exothermic, so that the progress of the reaction should be favored by lower temperatures. Data are not available to evaluate this tendency, but it has been noted in practice that excessive temperature in the reducing period may adversely influence chromium recovery.[6] For this reason, addition agents of low-silicon concentrations are used to good effect as the massive addition lowers steel temperature. Apart from the problem of slag reduction, it is desirable and frequently imperative to lower the bath temperature rapidly at the end of the oxidizing period to prevent serious refractory deterioration. Experimental determination of the temperature changes resulting from the solution of different types of silicon-bear-

Table I. Metallic Oxidation Data

Heat No.	Type	Size, Tons	Lining	End of Oxidation: Charge, Pct Cr	Charge, Pct Mn	Metal Analyses, Pct C	Metal Analyses, Pct Cr	Metal Analyses, Pct Mn	Metal Analyses, Pct Ni	Slag Analyses, Pct Cr_2O_3	Slag Analyses, Pct Met. Cr	Slag Analyses, Pct MnO	Slag Analyses, Pct FeO	Slag Analyses, Pct CaO	Slag Analyses, Pct MgO	Slag Analyses, Pct SiO_2	Slag Analyses, Pct Al_2O_3	Cr+Mn/Fe Slag, Pct Actual (S_1)	Cr+Mn/Fe Slag, Pct Est. (S_2)	Lb Cr+Mn+Fe Oxidized per Ton Actual (W_1)	Lb Cr+Mn+Fe Oxidized per Ton Est. (W_2)
1	303	15	Basic	16.00	0.64*	0.048	8.18	0.08	8.35	53.64	—	3.11	18.14	11.84	0.85	10.22	3.06	2.78	2.65	257	260
2	303	15	Basic	14.70	0.71*	0.068	9.46	0.11	8.12	45.68	—	3.29	30.37	8.74	0.77	9.39	2.32	1.43	3.02	237	178
3	304	15	Basic	15.00	0.70†	0.040	7.43	0.18	9.75	54.04	1.04	8.37	17.98	12.36	4.62	7.12	1.26	3.18	2.50	236	253
4	304	15	Basic	14.84	0.70†	0.046	9.24	0.17	9.21	50.97	1.81	7.20	16.28	14.02	8.17	10.26	1.72	3.34	3.00	181	167
5	304L	15	Basic	5.90	0.50†	0.010	0.32	0.01	14.53	11.63	—	1.22	46.84	22.24	4.23	7.08	1.23	0.245	0.191	627	773
6	304	25	Chromite	15.85	0.32*	0.040	9.77	0.07	10.08	63.65	1.38	2.17	16.67	1.63	3.62	6.62	5.98	3.60	3.15	185	192
7	304	25	Chromite	15.80	0.30*	0.073	11.57	0.22	10.44	21.23	1.35	0.43	5.82	26.02	28.72	12.26	1.40	3.59	3.74	130	128
8	304	1	Acid	17.40	0.95*	0.072	12.27	0.16	12.30	35.60	6.52	5.31	10.73	3.70	—	38.02	1.54	4.19	4.04	173	175
9	304L	1	Basic	12.02	0.68	0.014	4.51	0.03	14.95	31.69	0.97	12.07	18.07	5.94	13.51	18.24	7.58	2.28	1.68	251	281
10	CrMnNi	1	Basic	10.45	3.48	0.08	9.14	1.18	6.46	25.39	—	14.80	8.91	8.46	13.52	23.00	—	4.17	3.18	103	110
11	CrMnNi	1	Basic	10.90	2.94	0.07	7.92	0.81	6.22	15.15	—	7.49	6.47	13.35	37.32	19.36	0.60	3.21	2.73	151	158
12	CrMnNi	1	Basic	10.95	3.00	0.06	9.86	1.44	6.37	12.80	—	8.81	5.39	16.82	19.02	32.14	2.62	3.72	3.46	78	80
13	CrMnNi	1	Basic	10.71	3.11	0.08	9.02	1.45	6.31	15.05	—	11.51	5.42	20.41	21.69	19.94	2.52	4.56	3.24	94	102
14	CrMnNi	1	Basic	10.55	9.73	0.05	6.74	2.45	1.20	25.21	—	30.78	12.79	8.92	13.01	10.80	3.40	4.14	2.73	311	346

* Calculated from nickel balance.
† Estimated.

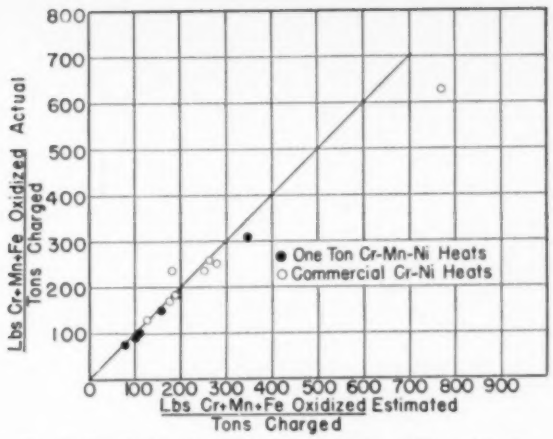

Fig. 2—Correlation of estimated and actual metallics oxidized.

ing alloys in the bath without chemical reaction is shown in Table II.

In 1950, Taylor[7] indicated a relation between chromium oxide, the slag basicity, and silicon in the metal. The ratio of CaO to SiO_2 was used as the index of basicity, and it was shown that high basicity favored reduction of chromium from the slag. Crafts and Rassbach included a preliminary evaluation of basicity and other factors related to the control of chromium oxide in the slag. Because of refractory erosion, significant amounts of magnesia are often present in these slags, and, therefore, this constituent was included in the basicity ratio which was expressed as the ratio of the sum of pct CaO + pct MgO to pct SiO_2. Data from a number of experimental heats and some commercial heats were used to illustrate the relation between slag basicity and slag chromium content. The heats used to establish these relations contained approximately 18 pct Cr, and the silicon contents varied from 0.30 to 1.00 pct. It was observed that the correlation of silicon content with slag chromium content for a given basicity was poor.

Shaw[8] showed a relation observed in commercial practice between the percentage of chromium in the slag converted to Cr_2O_3 and the ratio of CaO to SiO_2. The shape of the curve was similar to that shown by Crafts and Rassbach, and a comparison of the two curves suggested that the incorporation of MgO in the basicity factor would result in good agreement between the two sets of data. Shaw's data showed a variation of bath silicon contents from 0.10 to 0.54 pct, and there was little correlation between bath silicon content and chromium content of the slag for a given basicity.

Table II. Effect of Silicon-Bearing Alloys on Temperature

Composition of Addition Agent, Pct			Loss in Bath Temperature, °F, with Addition of 1 Lb of Silicon per Ton
Si	Cr	Fe	
6	65	25	30
45	39	15	2

It is evident from this review of some previous investigations that knowledge of the slag-reducing procedure is limited, and that a substantial portion of the data came from experimental heats. This new investigation includes some additional data from large commercial furnaces in an effort to extend further some of the basic relations in the slag-reduction period that are needed for closer process control.

Effect of Basicity on Recovery of Chromium

Additional information on the relation of unreduced metallic oxides to basicity was obtained from a number of heats representing a wide variety of operating conditions, as shown in Table III and illustrated in Figs. 4 and 5. Furnaces from which the

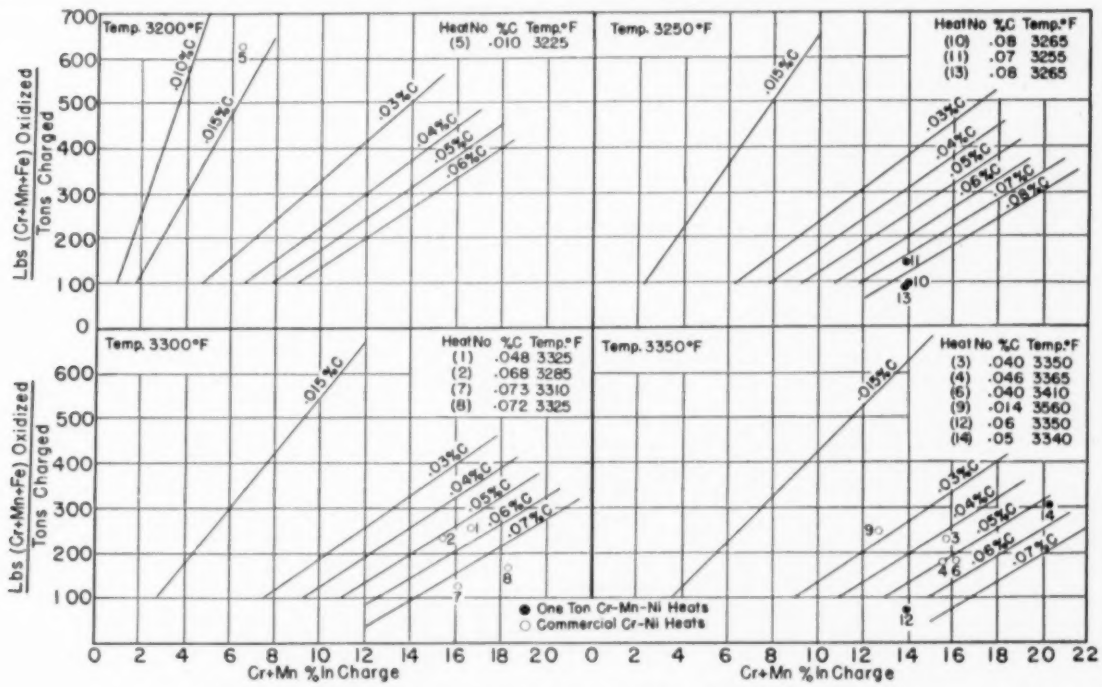

Fig. 3—Estimated metallics oxidized in decarburizing to various carbon contents.

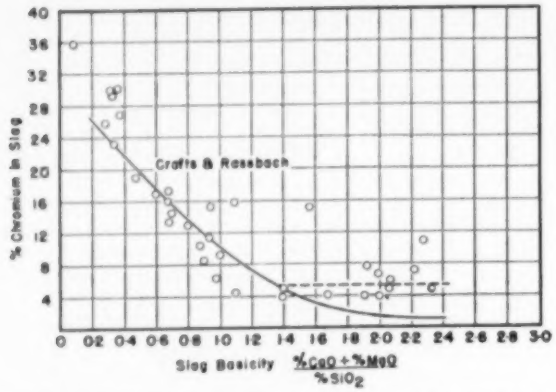

Fig. 4—Relation between chromium in slag and the basicity at end of reduction for commercial heats.

data were obtained varied in capacity from 7 to 75 tons, and the percentage of charged chromium ranged up to 15 pct. While most of the heats were from basic furnaces, some data from chromite hearth furnaces have been included and appear in the very low basicity range of the curves.

The solid lines in Figs. 4 and 5 are those established by Crafts and Rassbach based principally upon experimental data. While there is good general agreement of the new data with the old, it is significant that, in the basicity range of 1.4 to 2.2, slag chromium content and the sum of the metallic oxides in the slag remained constant instead of continuing to decrease as in the case of the experimental 1-ton heats. The new data, however, are consistent with those of Shaw when compared on a $CaO-SiO_2$ basicity ratio. It is, therefore, concluded that in large heats there is a significant deviation at high basicity from the experimental heats as indicated by the dotted lines in Figs. 4 and 5. While present knowledge of the chemistry of the process is too limited to provide an explanation of this behavior, it is a matter of observation that the small experimental furnace operates with less stratification in the bath and with more fluid slags than large furnaces with similar metal and slag compositions. This observed difference in operation may be due in part to major differences in the physical proportions of the furnaces. For example, the ratio of hearth area to bath depth and the ratio of electrode arc area to total slag area may have significance. This trend toward incomplete reduction of chromium oxide in large furnaces suggests that further experimentation with methods of improving slag-metal contact and slag fluidity may be desirable.

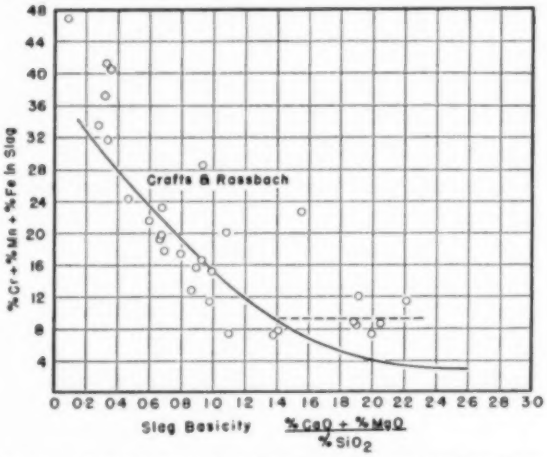

Fig. 5—Relation between Cr+Mn+Fe in slag and the basicity at end of reduction for commercial heats.

The previous studies of the influence of bath silicon concentration on slag chromium content for a given basicity showed poor correlation. Because it is believed that further investigation of this problem is warranted, data from a number of commercial heats covering a wide range of basicities, as shown in Table IV, have been plotted in Fig. 6. The heats used in this study contained from about 12 to 20 pct Cr and were in the range of 0.18 to 1.28 pct Si at the end of slag reduction. Fourteen of these heats con-

Table III. Slag Analyses at End of Reduction in Commercial Cr-Ni Heats

Heat No.	Lining	Size, Tons	Type	Si in Metal, Pct	Slag Analyses, Pct								CaO + MgO / SiO_2, Pct
					Cr_2O_3	Met. Cr	MnO	FeO	CaO	MgO	SiO_2	Al_2O_3	
15	Chromite	50	430	0.32	37.96	—	2.58	7.26	8.66	1.80	37.81	3.99	0.28
16	Chromite	50	430	0.07	52.50	—	2.66	11.69	1.14	1.24	26.04	5.01	0.09
17	Chromite	50	430	0.13	44.08	—	2.48	10.99	7.46	2.52	28.02	4.70	0.36
18	Chromite	50	430	0.51	39.32	—	2.42	4.38	9.94	2.88	24.50	6.80	0.37
19	Chromite	50	430	0.32	42.86	—	2.98	12.38	8.84	0.90	29.80	2.48	0.33
20	Chromite	50	430	0.16	43.85	—	2.83	11.99	8.00	1.42	29.14	2.58	0.32
21	Basic	75	430	0.34	25.57	—	4.42	2.82	18.81	7.60	38.94	1.45	0.68
22	Basic	75	430	0.07	22.20	—	2.14	7.22	24.57	13.05	25.32	3.46	1.56
23	Basic	75	18-6-4	0.33	22.36	—	11.48	5.26	23.72	5.36	30.76	1.18	0.94
24	Basic	75	18-6-4	0.27	23.27	—	1.80	3.43	26.32	9.90	33.10	2.53	1.09
25	Basic	75	302	0.38	13.43	—	5.29	2.47	24.32	12.91	37.10	4.12	1.00
26	Basic	75	302	—	19.51	—	3.99	4.41	21.41	6.66	41.30	2.52	0.68
27	Basic	7	302	0.18	7.19	—	—	—	34.57	11.20	22.30	—	2.05
28	Basic	7	347	0.40	6.21	—	—	—	32.20	11.62	26.00	—	1.68
29	Basic	7	316	0.19	15.95	—	—	—	32.63	11.72	19.49	—	2.27
30	Basic	7	316	0.39	7.25	—	—	—	37.80	15.69	23.06	—	2.32
5	Basic	15	304L	0.27	11.40	—	0.96	4.39	43.88	5.67	25.84	4.90	1.92
31	Basic	15	430	0.29	23.76	2.90	2.04	4.38	10.48	9.27	42.30	2.45	0.47
32	Basic	15	430	0.48	23.06	1.27	2.13	3.95	13.18	10.16	39.74	3.06	0.60
33	Basic	15	430	0.70	14.06	4.99	1.81	2.44	16.20	12.21	40.72	7.80	0.70
34	Basic	15	430	0.78	8.69	2.72	1.73	2.37	18.24	15.52	38.60	8.61	0.87
35	Basic	15	303	0.60	19.58	10.34	5.43	3.01	8.82	7.02	46.70	2.87	0.34
36	Basic	15	303	0.38	11.45	4.96	3.94	1.94	23.81	7.14	38.72	3.61	0.80
37	Basic	15	303	0.31	3.68	2.68	2.66	0.86	41.52	5.33	33.20	6.40	1.41
38	Basic	15	303	0.45	3.33	2.75	2.52	1.01	38.88	7.78	33.60	6.55	1.39
3	Basic	15	304	0.33	5.01	0.54	3.48	2.16	47.18	8.75	29.48	5.32	1.90
4	Basic	15	304	0.93	5.07	0.51	2.91	1.66	50.50	7.23	28.82	5.84	2.00
1	Basic	15	303	1.87	10.34	—	1.30	4.19	46.32	2.38	21.90	8.86	2.22
2	Basic	15	303	3.67	8.81	—	1.64	1.45	45.78	2.98	23.60	10.38	2.06
6	Chromite	25	304	1.25	6.58	11.35	2.05	2.66	22.20	4.55	39.58	7.82	0.67
7	Basic	25	304	1.74	7.75	1.19	0.67	1.94	39.26	16.21	29.36	3.04	1.89
39	Basic	65	304L	0.45	11.39	3.54	3.19	3.59	20.26	17.36	37.58	2.84	0.93
40	Basic	65	304L	0.70	6.53	1.71	4.13	2.73	22.12	14.80	40.30	2.50	0.96
41	Basic	75	304L	1.28	5.87	—	—	6.77	32.05	13.84	35.50	2.24	1.29
42	Basic	65	304L	0.66	10.80	1.01	2.40	6.89	30.77	3.33	38.04	3.82	0.90
43	Basic	65	304L	0.97	1.48	3.36	2.91	1.21	37.27	9.36	42.36	1.28	1.10

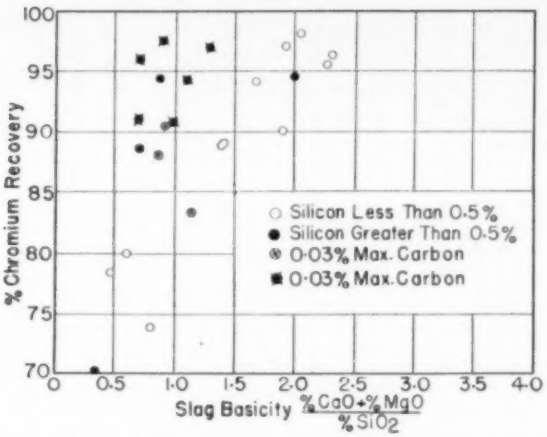

Fig. 6—Relation between chromium recovery and slag basicity at end of reduction for commercial heats.

tained a substantial amount of chromium in the initial charge, so that chromium was first oxidized and was then partially reduced by silicon. Ten of the heats were made for an 0.03 pct maximum carbon specification using chromium-free scrap charges. After the oxidation periods and in the presence of the iron oxide-rich slags, silicon-bearing ferrochromium was added. Loss of chromium resulted from partial oxidation and transfer of chromium into the slags in the presence of silicon. Equilibrium between the slag and metal with respect to chromium was, therefore, approached from both directions.

Although no close correlation was obtained with these data, several significant trends may be observed. It is notable that there was no appreciable difference between those heats in which chromium was present in the initial charge and those in which all the chromium was added after oxidation. This observation is of considerable interest, but its implications are not sufficiently well established to justify a conclusion that comparable chromium recoveries will be obtained under all conditions.

In heats with high-basicity slags, recovery was not greatly affected by silicon content. Heats made under the neutral slags, which minimize carbon pickup in melting low-carbon stainless steels, showed that high silicon aided chromium recovery. However, in the very low-basicity range, silicon concentration had little influence on chromium recovery. The effect of silicon content is also illustrated by Fig. 7 where silicon content after slag reduction is plotted against chromium recovery. This relation is quite complex and a need for further investigation is indicated.

Recovery of Manganese from Cr-Mn Steel Slags

Data from the five experimental 1-ton heats of high-manganese stainless steel listed in Table V are shown in Fig. 8 to illustrate the influence of basicity on chromium and manganese in the slag at the end of reduction. It is evident that for a given basicity

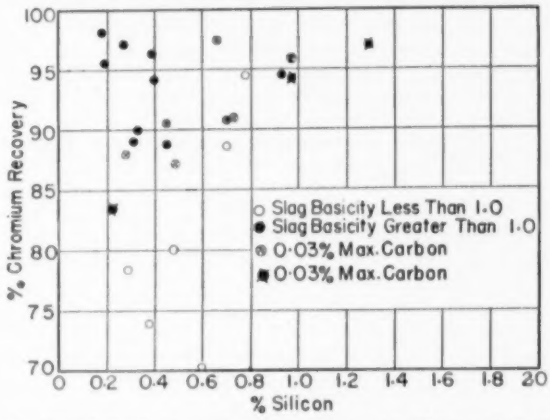

Fig. 7—Relation between chromium recovery and silicon content of the metal in commercial heats.

the manganese content of the slag was higher than that of chromium.

In the high-manganese heats the relation between chromium in the slag and basicity apparently followed closely that obtained on low-manganese heats, and, therefore, appeared to be unaffected by manganese in the slag. It may be inferred that good recovery of manganese from the slag depends upon a substantially higher basicity ratio than that required for chromium. For example, in the case of the heat, No. 14, having a basicity ratio of 1.75, the loss of chromium was 7.2 pct, whereas the loss of manganese in the slag was 29.5 pct. In the production of very high-manganese stainless steels, it appears that relatively high basicities are required to avoid excessive manganese losses.

Table IV. Data on Recovery of Chromium vs Pct Silicon and Slag Basicity

Heat No.	Type	Size, Tons	Chromium Added, Lb				Cr Lost in Slag			Metal Wt, Lb	Cr, Pct	Recovery of Cr		Si in Metal, Pct	Slag Analysis, Pct			
			Charge	FeCrSi	Simplex FeCr	Total	Slag Wt, Lb	Cr, Pct	Cr, Lb			Lb	Pct		CaO	MgO	SiO_2	"V"
44	304L	45	0			18,828				98,000	19.40	15,780	83.4	0.21	37.20	7.53	39.48	1.14
45	304L	45	0			21,905				98,200	19.40	19,050	87.0	0.48	18.00	11.20	33.40	0.87
46	304L	45	0			21,257				96,115	20.12	19,340	91.0	0.67	16.90	9.47	37.46	0.70
39	304L	65	236		22,167	22,403				113,850	17.81	20,276	90.5	0.45	20.26	14.80	37.58	0.93
47	304L	45	0		—	18,876				94,280	19.20	18,100	96.0	0.97	17.00	4.60	30.92	0.70
40	304L	65	173		22,752	22,925				110,650	18.78	20,780	90.8	0.70	22.12	17.36	40.30	0.98
41	304L	75	0		34,500	34,500				171,000	19.64	33,580	97.0	1.28	32.05	13.84	35.50	1.29
42	304L	65	0		25,441	25,441				125,420	19.76	24,783	97.4	0.66	30.77	3.33	38.04	0.90
43	304L	65	0		24,593	24,593				126,245	18.37	23,191	94.3	0.97	37.27	9.36	42.36	1.10
48	304L	25	0		9,539	9,539				48,300	17.59	8,500	88.1	0.27	20.00	11.96	37.20	0.87
31	430	15	4348			4,348				27,650	12.52	3,451	79.4	0.29	10.48	9.27	42.30	0.47
32	430	15	4348	655		5,003				28,250	14.18	4,006	80.0	0.48	13.18	10.16	39.74	0.60
33	430	15	4348	744		5,092				29,000	15.55	4,510	88.6	0.70	16.20	12.21	40.72	0.70
34	430	15	4348	886		5,234				31,100	15.91	4,948	94.5	0.78	18.24	15.52	38.60	0.87
35	303	15	4900	—		4,900				27,100	12.68	3,436	70.1	0.60	8.82	7.02	46.70	0.34
36	303	15	4868	655	—	5,523				27,550	14.81	4,080	73.9	0.38	23.81	7.14	38.72	0.80
37	303	15	4900	673	—	5,573				28,200	17.58	4,958	89.0	0.31	41.52	5.33	33.20	1.41
38	303	15	4895	709		5,604				28,600	17.61	5,036	88.8	0.45	38.88	7.78	33.60	1.39
3	304	15				5,096				27,300	16.81	4,589	90.0	0.33	47.18	8.75	29.48	1.90
4	304	15				6,056				29,800	19.22	5,727	94.6	0.93	50.50	7.23	28.82	2.00
49	302	7	2505	160		2,665	1000	4.92	49	—	—	2,616	98.2	0.18	38.47	11.20	22.30	2.05
50	347	7	2348	200		2,548	3500	4.25	149	—	—	2,399	94.2	0.40	32.20	11.62	26.00	1.68
51	316	7	2310	200		2,510	1005	10.92	110	—	—	2,400	95.6	0.19	32.63	11.72	19.49	2.27
52	316	7	2488	200		2,688	1955	4.96	97	—	—	2,591	96.4	0.39	37.80	15.69	23.06	2.32

Table V. Slag Analyses at End of Reduction of Cr-Mn-Ni in 1-Ton Heats

Heat No.	Composition, Pct			Si in Metal, Pct	Slag Analyses, Pct							$\frac{CaO+MgO}{SiO_2}$, Pct
	Cr	Mn	Ni		Cr_2O_3	MnO	FeO	CaO	MgO	SiO_2	Al_2O_3	
1	18	5	5	0.37	2.31	3.83	2.87	29.33	31.57	25.24	3.06	2.41
2	18	5	5	0.57	2.81	5.52	3.16	39.82	20.46	27.40	0.60	2.20
3	18	5	5	0.71	0.58	1.06	2.12	51.76	15.90	23.96	2.52	2.83
4	18	5	5	0.44	0.58	1.41	1.15	50.47	13.68	24.52	3.28	2.61
5	16	16	0.6	0.09	4.93	18.70	2.59	33.37	8.80	24.00	2.00	1.76

Silicon Usage in Slag Reduction

The amount of chromium plus manganese plus iron reduced per pound of silicon oxidized must be known to establish the reduction practice. In the previous investigation[5] the experimental heats showed an average of 3 lb of metal reduced per pound of silicon oxidized. The variation between individual heats was quite wide, a range of about 2.5 to 3.5 lb being observed.

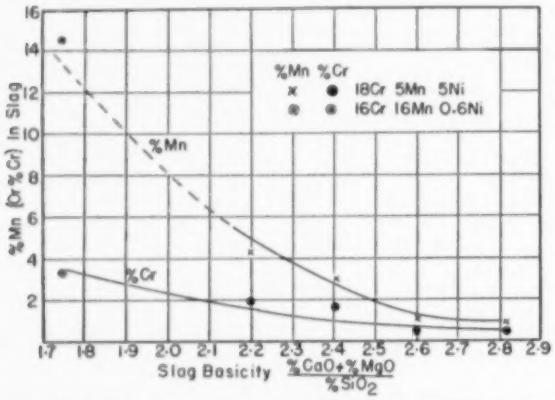

Fig. 8—Relation among manganese and chromium contents in the slag, and basicity at the end of reduction for experimental Cr-Mn-Ni heats.

An effort to develop information on commercial heats resulted in data from the four heats of 15 to 25 tons shown in Table VI. The chromium content of materials charged was known, and slag and metal analyses were obtained at the end of the oxidation period. Calculations on the basis of these data were made to determine the weight of metal oxidized. Information with respect to alloying additions, slag analyses and weights, final steel tapped weight, and composition made it possible to calculate the pounds of chromium plus manganese plus iron reduced per pound of silicon added. It was found that for these four heats the pounds of metal reduced per pound of silicon oxidized were 2.37, 2.53, 2.55, and 2.76. These results are within the range of the experimentally determined values and do not permit further generalization.

Estimation of Slag Weight

Since the amount of chromium lost in a slag is dependent on both the chromium concentration and the weight of the slag, control of slag weight at the end of reduction is of primary importance in chromium recovery. As was observed in Fig. 4, the data from large furnaces indicated a constant level of about 6 pct Cr at the end of reduction. This trend suggests that increasing basicity above 1.4 tends to decrease chromium recovery due to an increase in slag weight while maintaining the same chromium concentration. It is recognized also that large slag volumes result in unfavorable operating conditions and severe erosion of refractories. Estimation of slag weight, therefore, is of real interest in establishing chromium steel melting practices.

As part of the previous investigation,[5] Hilty described a technique for estimating slag weights. The assumptions made in those calculations were that 1 lb of silicon reduces 3 lb of chromium plus manganese plus iron (reduction factor) from the slag, and that 1 lb of these elements is equivalent to 1.29 lb of metallic oxides. Data from the four heats in Table VI were used to evaluate the accuracy of this method for calculating slag weights for commercial heats. Following the methods outlined by Hilty, a hypothetical table of the effects of graduated amounts of silicon oxidized upon the balance of the components of the slag was calculated for each heat. In each case the table was adapted to fit the actual conditions imposed by the heats. The quantities of slag components at the end of the oxidizing period were calculated from an estimation of metallic oxidation, as described earlier in this paper, and the known analysis of the slag. The remainder of the table was then calculated with the provision that the amounts of SiO_2, CaO, MgO, and Al_2O_3 ("non-reducible" oxides) should conform to the concentrations of these components in the actual slags after reduction. By interpolation from these tables it was

Table VI. Pounds Cr+Mn+Fe Reduced per Pound Silicon Oxidized

Heat No.	Cr+Mn+Fe Oxidized per Ton	Tons Charged	Total Cr+Mn+Fe Oxidized, Lb	Slag at End Reduction			Cr+Mn+Fe Reduced, Lb	Reducing Agent	Weight, Pct		Si Equiv., Pct*	Si Equiv., Lb*
				Weight, Lb	Cr+Mn+Fe, Pct	Cr+Fe+Mn, Lb						
3	236	13.8	3257	8,230	8.35	687	2570	FeCrSi #2	2500		44.6	1100
4	181	13.75	2489	7,330	7.51	550	1939	FeCrSi #2	2270		44.0	1000
								Simplex FeCr	1700		6.0	100
										Total		1100
6	185	23.03	4260	7,415	19.06	1458	2802	FeCrSi	3000		45.2	1356
								50% FeSi	350		48.0	168
								Al	68			53
										Total		1577
7	130	28.40	3692	11,015	8.69	957	2735	FeCrSi	3000		45.2	1356
								85% FeSi	300		85.0	255
								Al	67			52
										Total		1663

* Including the silicon stoichiometrically equivalent to the contained aluminum.

possible to estimate the amounts of silicon oxidized for each of the heats, and, by reference to the actual final slag compositions, to estimate the amounts of metallics reduced. The amounts of unreduced metal were then obtained by difference from the original amounts oxidized, and the slag weights were calculated from these quantities and the slag analyses. Comparison of these calculated weights with the actual weights are shown in Table VII. Although heats 3 and 4 were weighed quite accurately, the excellent agreement may be fortuitous since the reduction factor is known to vary considerably from heat to heat. Heat 7 had more than a normal amount of bottom erosion. The results suggest, however, that the technique described may be used to estimate slag volumes for commercial heats.

Summary

As part of a continuing program directed toward attaining improved production of stainless steel, a study was made to establish for commercial practice the validity of the relations previously derived from small, experimental heats. Primary emphasis was placed on data for the slag-reduction periods of commercial heats which were analyzed and compared with those from experimental heats in order to evaluate some of the factors which influence the recovery of chromium and manganese by silicon reduction of the oxidized slags resulting from decarburization.

Analytical data from the commercial heats of chromium-nickel steel confirmed the relationship, previously proposed from 1-ton heat data, which expressed the ratio of chromium plus manganese to iron in the slag as a function of the corresponding ratio of these elements in the metal after decarburization. The equivalence of manganese to chromium in this relationship was indicated by a similar correlation shown for data taken from 1-ton, Cr-Mn-Ni heats with high manganese (5 to 10 pct) in the charge. The calculated metallics oxidized, based upon actual slag analyses, were in excellent agreement with predicted values for both the commercial and the 1-ton heats used in this study.

The relation of basicity to chromium in the slag after reduction was compared with the previously developed relation which was based largely on data from experimental heats. The comparison showed a marked deviation in that chromium and the sum of metallic oxides remained constant in the range of 1.4 to 2.2 basicity suggesting that basicities above 1.4 have limited value for increasing recovery of chromium.

Table VI. Continued.

Heat No.	Bath Weight, Lb	Si, Pct	Si Alloyed, Lb	Si Oxid., Lb	Cr + Mn + Fe Reduced/ Si Oxid., Lb
3	27,300	0.33	91	1009	2.55
4	29,800	0.93	277	823	2.37
6					
7	48,300	0.97	469	1108	2.53
	57,000	1.18	673	990	2.76
				Average	2.55

Table VII. Calculated Slag Weights

Heat No.	Type Hearth	Slag Weight After Reduction in Lb of Slag per Ton of Metal	
		Calculated	Actual
3	Basic	615	602
4	Basic	486	492
6	Chromite	279	305
7	Basic	470	387

Study of the influence of silicon in the metal on recovery of chromium at the end of the reduction period showed that unusually high concentration of silicon is not necessary for good recovery from high-basicity slags. At low basicities, however, relatively poor recovery of chromium was realized even at high-silicon contents. In the neutral range, which is desirable for controlling carbon pickup in melting the very low-carbon stainless steels, silicon in the metal after reduction had a strong influence on chromium recovery.

Comparison of slag-metal relations of commercial heats containing substantial amounts of chromium in the initial charge with those of heats in which no chromium was charged and in which the iron-rich slag was partially reduced with a silicon-bearing chromium alloy showed similar overall chromium recoveries with about the same conditions of basicity and silicon concentration. This observation provided an indication that equilibrium between slag and metal with respect to chromium is approached rapidly from both directions. A corollary to this conclusion is that in scrap heats in which part of the chromium is included in the charge and part is added while the slag is being reduced, the chromium from the initial charge remaining in the slag tends to be lowered as a result of furnace conditions, and, therefore, chromium from the late addition is not lost to the slag.

Experimental heats of high manganese-chromium-nickel steels showed that for a given slag basicity after reduction the manganese content of the slag was higher than that of chromium but that the general dependence of manganese concentration on basicity was similar to that observed for chromium. The presence of manganese in the slag had no appreciable influence on the reduction of chromium, so that a slag that is sufficiently basic to insure good chromium recovery may not be sufficiently basic to yield good manganese recovery.

Observations of the amount of metal reduced from the slag per pound of silicon oxidized for commercial heats were within the range of those previously made on experimental heats. There is need, however, for additional data to achieve better understanding of reasons for the wide variations in this reduction factor.

A method for calculating slag weight was demonstrated to be suitable for use in the appraisal of the practicability and economic aspects of a proposed melting practice. Since it is predicated upon a material balance with respect to slag-metal reactions, it provides a basis for checking the overall accuracy of the oxidation and reduction methods proposed.

Acknowledgments

The authors wish to express their appreciation to Walter Crafts, Associate Director of Research, and D. C. Hilty, Research Metallurgist, of the Union Carbide and Carbon Research Laboratories, Inc., for their very generous and valuable cooperation. It is evident that this study was made possible through

the aid of stainless steel producers in providing the necessary data. This assistance is acknowledged with grateful appreciation.

References

[1] D. C. Hilty: Relation between Chromium and Carbon in Chromium Steel Refining. *Trans.* AIME (1949) **185**, pp. 91-95; JOURNAL OF METALS (February 1949).

[2] D. C. Hilty, G. W. Healy, and W. Crafts: Metallic Oxidation in Chromium Steel Melting. *Trans.* AIME (1953) **197**, pp. 649-653; JOURNAL OF METALS (May 1953). Abstracted by D. J. Girardi and D. C. Hilty: Oxygen in Steelmaking. JOURNAL OF METALS (July 1952) p. 705.

[3] W. Crafts and H. P. Rassbach: Melting Low-Carbon Stainless Steel. *Electric Furnace Steel Proceedings*, AIME (1951) **9**, pp. 95-104.

[4] D. C. Hilty: High-chromium Steel in the Acid Arc Furnace. *Electric Furnace Steel Proceedings*, AIME (1949) **7**, pp. 95-104.

[5] J. E. Harrod: Discussion on ref. 3. *Electric Furnace Steel Proceedings*, AIME (1951) **9**, pp. 104-106.

[6] B. R. Queneau and A. C. Ogan: Stainless Steel Melting Practices Have Changed. *Iron Age* (Dec. 4, 1952) pp. 165-169.

[7] C. R. Taylor: Some Observations on the Metallurgy of Electric-furnace Melting. *Electric Furnace Steel Proceedings*, AIME (1950) **8**, pp. 91-97.

[8] R. B. Shaw: Discussion on ref. 3. *Electric Furnace Steel Proceedings*, AIME (1951) **9**, pp. 106-107.

Technical Note

Thermal Conductivity of Nodular Iron

by M. J. Sinnott

WITH the advent of nodular iron as an engineering material, considerable interest has been shown in developing this material for various applications. Generally the strength, hardness, or ductility are the more common properties used for design purposes but occasionally applications involving a knowledge of the thermal conductivity of the material is required. A search of the literature showed, rather surprisingly, that relatively little work has been done on this property for all types of cast iron. Insufficient data are available on thermal and electrical conductivities to develop the Weidemann-Franz ratio, or the Lorentz relationship, for estimation purposes. There are no data on nodular irons and the published data on malleable irons are quite sketchy. For these reasons the conductivity of the group of nodular irons listed in Table I were measured.

Table I. Chemical Composition of Nodular Irons

Iron	Total C	Si	Mn	S	P	Ni	Mg
I	3.57	1.12	0.33	0.004	0.035	1.33	0.06*
II	3.56	2.27	0.33	0.010	0.025	1.30*	0.06*
III	3.47	3.53	0.29	0.012	0.030	1.30*	0.06
IV	3.36	4.34	0.40	0.010	0.030	1.23	0.06
V	3.33	2.28	0.50	0.010	0.055	1.12	0.06

* Estimated.

Irons I to IV were made in such a fashion as to maintain the carbon and alloy content essentially the same while varying the silicon content. Test specimens were cut from the mid-section of 4-in. keel castings. Iron V is a commercial casting of nodular iron. The test specimen of this iron was cut from the center of a large cast billet 3x10x26 in. All alloys were tested in the as-cast condition. A microstructural examination showed that each iron had spheroidal graphite but the size and distribution varied with the silicon content of the iron. The spheroid size decreased while the number of graphite nodules increased as the silicon content of the iron was increased. The matrix structures of each iron consisted of pearlite and ferrite with the proportions varying from predominantly pearlite in the low-silicon iron to mostly ferrite in the high-silicon iron. The commercial heat, iron V, was predominantly pearlite probably because of its higher manganese and phosphorus content.

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Two methods for measuring the thermal conductivity were used. The first was a modification of the techniques described by Powell and Hickman[1] and Van Dusen and Shelton,[2] the second method was a simpler technique described by Jakob and Hawkins.[3] Since the agreement of both methods as tested on two sets of duplicate samples was excellent, the simpler experimental technique was used. The results of the measurements are given in Table II along with a summary of the microstructural constituents.

Table II. Thermal Conductivity and Microstructures of Nodular Irons

Iron	Thermal Conductivity, Btu/Hr-Ft²-Ft/°F (210° to 160°F)	Pearlite, Pct	Ferrite, Pct	Graphite, Pct	Graphite Size, In. x 100
I	21.8	61	30	9	0.186
II	21.5	40	50	10	0.121
III	20.9	35	55	9	0.096
IV	20.3	5	85	10	0.081
V	20.6	85	5	10	0.175

These conductivity data indicate that as the percentage of silicon increases there is a corresponding decrease in the thermal conductivity even though the structure is changing from pearlitic to ferritic. Such a change in microstructure is usually accompanied by an increase in conductivity.[4] A third factor involved in the behavior of these irons is the size and distribution of the graphite nodules. The relative amounts of graphite do not change greatly but the size and distribution do. Generally graphite improves the conductivity but in the present case such an effect is probably masked by the alloying effect from the silicon and its dispersion through the matrix.

The thermal conductivity of the nodular irons studied is less than that of regular foundry irons by some 10 to 30 pct and is less than that of regular malleable irons.[4] The cause of the decreased conductivity is probably the more highly alloyed ferrites obtained in these irons and the changed mode of distribution of the graphite as compared to the regular foundry irons.

References

[1] R. W. Powell and M. J. Hickman: *Journal* Iron and Steel Inst. (1946) **154**, No. 2, p. 99.

[2] M. S. Van Dusen and S. M. Shelton: U. S. Bur. Standards *Journal of Research*, RP668 (1934) **12**, p. 429.

[3] M. Jakob and G. A. Hawkins: *Elements of Heat Transfer and Insulation*. 2nd Ed. (1950) New York. John Wiley and Sons.

[4] J. W. Donaldson: *Journal* Iron and Steel Inst. (1933) **128**, No. 2, p. 255.

Silicon-Oxygen Equilibrium in Liquid Iron — A Revision

by John Chipman and Nev A. Gokcen

A revised treatment of the authors' published data eliminates the complex relation previously proposed between concentration of silicon and activity coefficient of oxygen in liquid iron. Revised values of the thermodynamic properties of the liquid solution are presented.

IN a recent experimental study of the reaction

$$SiO_2\ (s) = \underline{Si} + 2\underline{O};\ K'_1 = [\%\ Si]\ [\%\ O]^2 \quad [1]$$

the authors[1] found a substantially constant equilibrium product in liquid iron at 1600°C of 2.8×10^{-3}.

They also reported extensive data on the reactions:

$$SiO_2\ (s) + 2H_2\ (g) = \underline{Si} + 2H_2O\ (g);$$

$$K'_2 = [\%\ Si]\left(\frac{H_2O}{H_2}\right) \quad [2]$$

and

$$H_2\ (g) + \underline{O} = H_2O\ (g);\ K'_3 = \frac{(H_2O)}{(H_2)\ [\%\ O]} \quad [3]$$

From the results on reaction 3 and earlier data of Dastur[2] on this same reaction in the absence of silicon, they determined the activity coefficient of oxygen, f_o, on the basis of the definition $K_3 = (H_2O)/(H_2)f_o\ [\%\ O]$ where K_3 is the equilibrium constant and f_o is taken as unity in the pure Fe-O system. Similarly values of f_{si} were deduced from results on reaction 2.

In a more recent study[3] of analogous reactions in the system Fe-Al-O, it was found impossible to reconcile the results on reaction 3 with Dastur's data; accordingly the latter were ignored and the equilibrium results were extrapolated to find a value of K_3 at zero concentration of aluminum. This procedure failed to locate the cause of the discrepancy but it did yield reasonable values of activity coefficients. It also avoided introduction of the complex empirical relation between the oxygen activity coefficient and the concentration of the added element.

The same type of discrepancy exists for system Fe-Si-O.[1] In the earlier paper an attempt was made to fit both sets of data by a single curved line (Fig. 6 of ref. 1), the form of which is contrary to the theoretical requirement of a finite slope at infinite dilution. In the light of experience on the Fe-Al-O system the discrepancy must be recognized as one which can be resolved only by more refined measurements. Accordingly Figs. 6 and 10 are retracted. It is pointed out also that until the discrepancy is resolved Figs. 7, 8, and 11 are subject to some uncertainty.

Qualitatively the following conclusions still appear valid: 1—The activity coefficient of oxygen is reduced by addition of silicon. 2—In dilute solutions the activity coefficient of silicon increases with its concentration. 3—With respect to equilibrium in reaction 1, the above effects are approximately compensating.

The discussion of K'_1 in the previous paper requires no revision. It was pointed out that the constancy of the product $[\%\ Si]\ [\%\ O]^2$ indicated a compensating effect of the activity coefficients of silicon and oxygen. Therefore, as a very good approximation, $K_1 = K'_1$ and the following average values are suggested both for K_1 and K'_1 at the temperatures 1550°, 1600°, and 1650°, respectively, 1.0×10^{-3}, 2.8×10^{-3}, and 5.5×10^{-3}.

Revision of the thermodynamic treatment is necessitated by the recent appearance of new data, based on a combination of combustion and solution calorimetry,[4] which yields for the heat of formation of low-cristobalite from the elements, the value −209,330 ±250 cal per mol at 25°C. This is about 4000 cal larger than the value previously accepted. The new value for cristobalite is used, together with Kelley's tables of high-temperature heat contents[5] and entropies[6] and with Körber and Oelsen's[7] heat of fusion of silicon to obtain the following equation for the standard free energy of cristobalite in the temperature range 1700° to 2000°K:

$$Si\ (l) + O_2\ (g) = SiO_2\ (crist.);$$

$$\Delta F^\circ = -217{,}700 + 47.0T \quad [4]$$

The free energy of solution of O_2 in liquid iron is:[8]

$$O_2\ (g) = 2\underline{O}\ (\text{in Fe});\ \Delta F^\circ = -55{,}860 - 1.14T \quad [5]$$

and these two equations are combined to give:

$$Si\ (l) + 2\underline{O} = SiO_2\ (crist.);$$

$$\Delta F^\circ = -161{,}840 + 48.14T \quad [6]$$

$$\Delta F^\circ_{1873} = -71{,}700\ \text{cal.}$$

From the experimental value of $K_1 = 2.8\times10^{-3}$,

$$\underline{Si} + 2\underline{O} = SiO_2\ (crist.);\ \Delta F^\circ_{1873} = -39{,}000\ \text{cal.} \quad [7]$$

The combination of Eqs. 6 and 7 yields the free energy change when liquid silicon dissolves in iron to form the dilute solution of unit activity (1 pct).

$$Si\ (l) = \underline{Si};\ \Delta F^\circ_{1873} = -32{,}700\ \text{cal.} \quad [8]$$

The heat effect in this process according to Körber and Oelsen[7] is an evolution of 28,500 cal per gram

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atom. The difference falls into an entropy term to yield the equation:

$$\underline{Si}\ (l) = \underline{Si};\ \Delta F^\circ = -28{,}500 - 2.23T \qquad [9]$$

A similar but not identical result could be obtained from the observed value of K_2 and the free energy of water vapor. The above calculation, however, is probably more dependable and is consistent with all previous studies of oxygen in iron.

Combination of Eqs. 6 and 9 gives:

$$\underline{Si} + 2\underline{O} = SiO_2\ (crist.);$$
$$\Delta F^\circ = -133{,}340 + 50.37T \qquad [10]$$
$$\log K_1 = -29{,}150/T + 11.01$$

According to this equation the values of K_1 at 1550°, 1600°, and 1650° are 1.05×10^{-5}, 2.8×10^{-5}, and 7×10^{-5}, respectively. This is in fair agreement with the average observed values.

Eq. 9 may be further used to obtain γ° for silicon in very dilute solution in liquid iron. This is the value which is approached by the ratio of activity to mol fraction when the latter approaches zero. From Eq. 16-10 of *Basic Open Hearth Steelmaking*:[8]

$$Si\ (l) = \underline{Si};\ \Delta F^\circ = +4.575T \log\ (0.5585\ \gamma^\circ/28.06)$$

From this and Eq. 9 it follows that:

$$\log \gamma^\circ = -6230/T + 1.213 \qquad [11]$$
$$\gamma^\circ_{1873} = 0.0077$$

This is smaller than the value 0.017 previously reported.[9] The difference results from the new higher heat of formation of cristobalite and the lower value of K_1 found in this study.

Summary

The authors' previously published results[1] on equilibrium in the Fe-Si-O system are reviewed. Previous conclusions regarding activity coefficients in the liquid solution now appear unjustified. Values of the deoxidation product [% Si] [% O]^2 in the earlier paper provide the best estimates of the true equilibrium constant.

A newly published value of the heat of formation of cristobalite is used with the equilibrium results to revise the thermodynamic data for the dilute solution. Referring to *Basic Open Hearth Steelmaking*,[10] Eq. 16-11 should be replaced by Eq. 9; Eq. 16-27 by Eq. 4, and Eq. 16-29a by Eq. 10. Figs. 16-7, 16-20, and 16-29 are substantially unaffected by the revision.

References

[1] N. A. Gokcen and J. Chipman: *Trans.* AIME (1952) **194**, p. 171; JOURNAL OF METALS (February 1952).

[2] M. N. Dastur and J. Chipman: *Trans.* AIME (1949) **185**, p. 441; JOURNAL OF METALS (August 1949).

[3] N. A. Gokcen and J. Chipman: *Trans.* AIME (1953) **197**, p. 173; JOURNAL OF METALS (February 1953).

[4] G. L. Humphrey and E. G. King: *Journal* ACS (1952) **74**, p. 2041.

[5] K. K. Kelley: U. S. Bur. Mines *Bull.* 476 (1949).

[6] K. K. Kelley: U. S. Bur. Mines *Bull.* 477 (1950).

[7] F. Körber and W. Oelsen: *Mitt. Kaiser Wilhelm Inst. Eisenforschung* (1936) **18**, p. 109.

[8] *Basic Open Hearth Steelmaking.* 2nd Edition (1951) pp. 638-640. AIME.

[9] J. Chipman: Discussions, Faraday Soc. No. 4 (1948) p. 23.

[10] Ref. 8, p. 659.

Corrections

In the July 1953 issue, *Further Studies of the Tuyere Zone of the Blast Furnace* by J. B. Wagstaff, p. 896: Fig. 1 is printed upside down.

In the June 1953 issue, *Concentration Gradients Associated with Growing Pearlite* by Richard E. Grace: page 820, the caption for Fig. 1 should read: Electron micrograph of pearlite and martensite tempered 5 min, 0.9 pct C steel. X20,000. Page 820, first column, second paragraph, the eleventh line should read, in part: chromium at about 65° from the horizontal.

In the August 1952 issue, *Concentration Dependence of Diffusion Coefficients in Metallic Solid Solution* by Donald E. Thomas and C. Ernest Birchenall: page 870, Table I as printed below should be substituted for Table I in the paper. The authors are grateful to Dr. T. Heumann of the University of Münster for pointing out the error in Table I. Page 871, first column, the following paragraphs should be substituted for the two paragraphs preceding "Discussion":

Table I also includes the marker movements observed by da Silva and Mehl for pure nickel vs pure copper couples C4 and B38. In the former the marker was at 80.5 atomic pct Cu and in the latter at 71.0 atomic pct.

Following the method of Darken,[14] the diffusion coefficients of the individual components were calculated at the average marker composition. Although there is no clear trend of the ratio of D_{Cu} to D_{Ni} with temperature, the decrease in the ratio with decreasing copper concentration may be real.

Table I. Marker Displacements and Diffusion Coefficients in Cu-Ni Alloys

Temperature, °C	Sample	x_m, Cm	$2\sqrt{t}$, Sec$^{1/2}$	dN/dx, Cm^{-1}	D_{Cu}, Cm^2 per Sec	D_{Ni}, Cm^2 per Sec	D_{Cu}/D_{Ni}
1049	2	0.0056	6.61×10^{5}	6.4	1.6×10^{-9}	3.7×10^{-10}	4.3
1022	13	0.0079	1.16×10^{6}	5.1	1.6×10^{-9}	2.8×10^{-10}	5.7
	20	0.0079	1.16×10^{6}	4.5	1.9×10^{-9}	3.4×10^{-10}	5.6
975	17	0.0043	8.95×10^{5}	7.9	8.0×10^{-10}	1.8×10^{-10}	4.4
924	3	0.0051	3.63×10^{6}	6.0	3.0×10^{-10}	6.8×10^{-11}	4.4
	11	0.0051	3.63×10^{6}	5.9	3.0×10^{-10}	6.2×10^{-11}	4.8
922	6	0.0058	5.83×10^{6}	5.0	2.7×10^{-10}	6.7×10^{-11}	4.0
	16	0.0071	5.83×10^{6}	4.8	3.1×10^{-10}	6.4×10^{-11}	4.8
1054	C4*	0.0140	2.25×10^{6}	6.4	1.4×10^{-9}	4.2×10^{-10}	3.3
947	B38†	0.0039	2.60×10^{6}	29.	1.1×10^{-10}	5.5×10^{-11}	2.0

* Composition at marker interface — 80.5 atomic pct Cu.
† Composition at marker interface — 71.0 atomic pct Cu.
All others—Composition at marker interface — 89.9 atomic pct Cu.

Thermodynamic Properties of Molybdenum Dioxide

by Nev A. Gokcen

THE data of Chaudron,[1] Tonosaki,[2] and Collins[3] on the thermodynamic properties of MoO_2 disagree widely. These authors, by using essentially similar methods, studied the following reaction:

$$\tfrac{1}{2}MoO_2(s) + H_2(g) = \tfrac{1}{2}Mo(s) + H_2O(g), K = \frac{P_{H_2O}}{P_{H_2}} \quad [1]$$

Tonosaki used a vacuum system consisting of a furnace containing MoO_2 and a water saturator whose temperature was kept at 25°C with a thermostat. After repeated evacuation, hydrogen was admitted slowly into the system. The experiments were based upon the fact that at a constant furnace temperature and constant partial pressure of water, the total pressure of gas mixture over MoO_2 + Mo is constant. Any attempt to vary the pressure by external forces would vary only the amounts of MoO_2 and Mo, after which the pressure should return to the equilibrium value in accordance with the equilibrium constant of reaction 1. The actual value of K was determined from the total equilibrium pressure (sum of P_{H_2O} + P_{H_2}) at each temperature. The total pressure of gas was varied within the range of 80.2 to 125.4 mm Hg, within a temperature range of 645° to 823°C. The results were summarized as $\log K = 0.9413 - 1444.6/T$ for reaction 1. The ratio of H_2O/H_2 was considered to be uniform in spite of the presence of a thermal gradient across the static gas phase. It was shown by Rosenqvist and Cox,[4] however, that in somewhat similar circumstances the error resulting from thermal diffusion may be large.

Collins[3] improved Tonosaki's method by attempting to avoid thermal diffusion errors. His equilibrium data were obtained at 700°, 800°, and 900°C, and the result for reaction 1 was expressed as $\log K = 1.258 - 1822/T$.

The purpose of this investigation was to study reaction 1, avoiding the thermal diffusion errors, and to obtain equilibrium data in a considerably wide temperature range for the reliable extrapolation of the resulting thermodynamic functions.

Experimental Procedure

The diagram of the apparatus is shown in Fig. 1. Tank hydrogen was passed through a tube containing platinized asbestos at 425°C in order to convert a trace of oxygen into water vapor. The flow rate was carefully controlled with a capillary-type flowmeter B and a bubbling column D. The gas was then presaturated sufficiently at P and led into a condenser system immersed in a thermostat, controlled to within ±0.002°C. The temperature of the thermostat was measured with a thermometer calibrated against a certified standard. The temperature of P was adjusted to avoid the condensation of unduly large amounts of water as judged from the rate of flow out of the capillary tube M.

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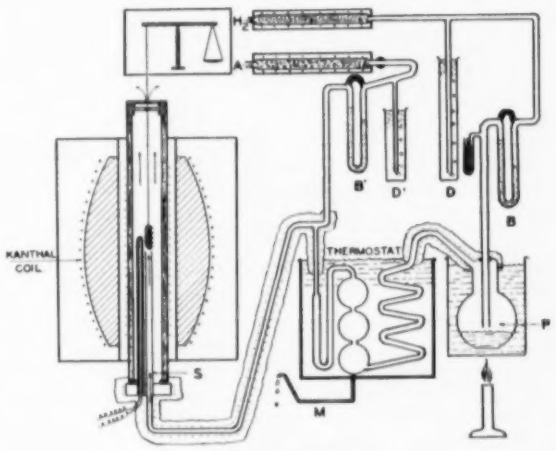

Fig. 1—Apparatus.

Argon was purified[5] by passing it through magnesium chips kept at 630°C. After passing through the flowmeter B', it was mixed with moist hydrogen emerging from the thermostat. The resulting gas mixture was then led into the hot zone of the furnace through the heated glass tubing and the silica tube S, thus insuring the same ratio of P_{H_2O}/P_{H_2} from the condenser to the reaction chamber, thus avoiding thermal diffusion. The entire gas system was of all-glass construction, except at the magnesium train.

The furnace comprised a glazed alumina tube over which a 15-in. platinum coil was wound. The lower end of the alumina tube was tightly closed with a brass bottom and a silicone rubber gasket, and the upper end with two glass disks, each with a hole of 1/16 in. in diameter, through which the gas mixture escaped into the atmosphere. A back-up coil of kanthal wire facilitated the temperature control of the furnace. A coil of annealed molybdenum strip of 99.99 pct purity, 0.005 in. thick and 0.050 in. wide, and weighing 17 g was hung in the furnace with a 0.010-in. platinum wire attached to one end of a sensitive analytical balance. The temperature of the furnace was measured with a Pt-Pt-10 pct Rh thermocouple checked against a standard.

The experimental procedure consisted of heating the gas purification trains, adjusting the gas flow rates, attaining a constant thermostatic temperature, flushing the entire system for 2 hr while heating the furnace to well above the expected equilibrium temperature and then cooling it at a rate of 0.3°C per min during which time the change in the weight of molybdenum was observed on the balance. For a given thermostatic temperature, i.e., a constant P_{H_2O}/P_{H_2}, molybdenum oxidized upon cooling slightly below the equilibrium temperature. The procedure was then repeated by heating the furnace and thus reaching a temperature slightly above the equilibrium value. The average of the two temperatures, differing by 2° to 3°C, was considered to be the true equilibrium temperature.

In order to determine the stoichiometric composition of the oxide phase present in this investigation,

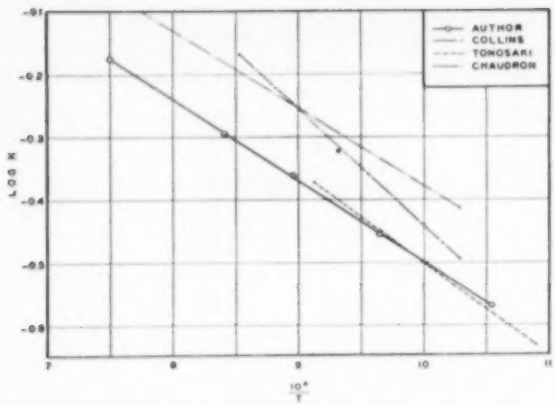

Fig. 2—Variation of the equilibrium constant $K = P_{H_2O}/P_{H_2}$ with temperature.

the loss of oxygen from a known amount of pure molybdenum trioxide (chemically pure MoO_3), contained in a suspended platinum crucible, was determined at 700°C under the experimental conditions in which an oxide was the only stable phase. The loss of oxygen indicated that the composition of this phase was MoO_2.

Results

The results are summarized in Table I. The value of P_{H_2O} corresponding to each thermostatic temperature was found from a recent steam table and corrected for a small deviation from ideality; the values of P_{H_2} were determined from the barometric pressure over the apparatus, minus P_{H_2O}, and the resulting ratios of P_{H_2O}/P_{H_2} are tabulated in the fourth column.

The data are plotted in Fig. 2 together with the lines of Chaudron, Tonosaki, and Collins. The results may be summarized by the following equation:

$$\log K = -\frac{1297}{T} + 0.798 \qquad [2]$$

The experiments show that the addition of argon did not affect the results from the point of view of thermal diffusion.[5, 6]

Thermodynamic Calculations

From Eq. 2, the standard free energy change is expressed as

$$\Delta F^\circ = 5935 - 3.65T, \text{ for} \qquad [3]$$
$$\tfrac{1}{2}MoO_2(s) + H_2(g) = \tfrac{1}{2}Mo + H_2O$$

This expression is sufficiently accurate within the range of temperatures not too far above or below the investigated limits of 949° and 1396°K. The extrapolation of ΔF° and ΔH° values of this equation to room temperature can be accomplished by the use of ΔCp for reaction 1. Heat capacity of MoO_2 is not known, but it may be estimated as 17.6 in the range of 298° to 900°K on the basis of comparison of the available Cp values for the dioxides of metals, i.e., UO_2, MnO_2, and PbO_2, and by considering Kopp's rule. Heat capacity of other substances in reaction 1 are given by Kelley.[7] Combination of Cp functions yields

$$\Delta Cp = -5.41 + 2.43 \times 10^{-3} T - 0.04 \times 10^5 T^{-2}$$

Contribution from the last term is very small, hence it may be disregarded. By using ΔCp, and the values of ΔH° and ΔF° at 900°K from Eq. 3, the following functions, valid from 900° to 298°K, are obtained:

$$\Delta H^\circ = 9824 - 5.41T + 1.21 \times 10^{-3} T^2 \qquad [4]$$
$$\Delta H^\circ_{298} = 8320 \text{ cal}$$
$$\Delta F^\circ = 9824 + 12.44T \log T - 1.21 \times 10^{-3} T^2 - 43.63T \qquad [5]$$
$$\Delta F^\circ = 5888 \text{ cal}$$
$$\Delta S^\circ_{298} = 8.16$$

The absolute entropy of MoO_2 at 298°K, $S^\circ_{298} = 18.3$ E.U., is calculated from $\Delta S^\circ_{298} = 8.16$ and the absolute entropies of $H_2(g)$, $H_2O(g)$, and Mo(s) compiled by Rossini, et al.[8]

The ΔH° and ΔF° functions for $2H_2(g) + O_2(g) = 2H_2O(g)$, obtained from the recent references,[7, 8] are combined with Eqs. 4 and 5 to express the standard free energy and heat of formation of MoO_2 in the range of 298° to 900°K:

$$Mo(s) + O_2(g) = MoO_2(s) \qquad [6]$$
$$\Delta H^\circ_f = -133{,}504 + 4.96T - 1.14 \times 10^{-3} T^2 - 0.32 \times 10^5 T^{-1} \qquad [7]$$
$$\Delta H^\circ_{f298} = -132{,}234 \text{ cal}$$
$$\Delta F^\circ_f = -133{,}504 - 11.384T \log T + 1.14 \times 10^{-3} T^2 - 0.16 \times 10^5 T^{-1} + 69.806T \qquad [8]$$
$$\Delta F^\circ_{f298} = 121{,}050 \text{ cal}$$

The value of ΔH°_{f298} agrees very closely with the calorimetric value of −130,000 reported by Mixter.[9]

In the range of steelmaking temperatures, ΔF° for reaction 6 is obtained by combining Eq. 3 with $\Delta F^\circ = -120{,}380 + 27.80T$ for $2H_2 + O_2 = 2H_2O$:

$$\Delta F^\circ = -132{,}250 + 35.1T \qquad [9]$$

Table I. Equilibrium Data for Reaction $\tfrac{1}{2}MoO_2 + H_2 = \tfrac{1}{2}Mo + H_2O$

Run No.	Hydrogen Flow Rate, Millimol per Min	Ratio, H_2/Argon	$K = P_{H_2O}/P_{H_2}$	Furnace Temperature, °C	Equilibrium Temperature, °C
2	7.50	2.20	0.5062	915* 917	916
3	7.50	1.97	0.4342	843* 845	844
4	7.50	2.20	0.3483	764* 767	765
5	6.70	3.35	0.2700	675* 677	676
6	3.10	0.94	0.6663	1060* 1061	1061
	3.10	0.44			

* Temperature at which oxidation began upon cooling; other refers to reduction.

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References

[1] Chaudron: *Ann. Chim.* (1921) **16**, p. 221.
[2] Tonosaki: *Bull.* Inst. Phys. Chem. Res., Tokyo (1940) **19**, p. 126.
[3] Collins: Sc. D. Thesis, Massachusetts Institute of Technology (June 1949).
[4] Rosenqvist and Cox: *Trans.* AIME (1950) **188**, p. 1389; JOURNAL OF METALS (November 1950).
[5] Gokcen and Chipman: *Trans.* AIME (1952) **194**, p. 171; JOURNAL OF METALS (February 1952).
[6] Dastur and Chipman: Discussions, Faraday Soc. (1948) No. 4, p. 100.
[7] Kelley: U. S. Bur. Mines, *Bull.* 476 (1949).
[8] Rossini, et al.: Circular 500, Nat. Bur. of Standards (1952).
[9] Mixter: *American Journal of Science* (1910) **29**, p. 488.

Influence of Aluminum and Silicon Deoxidation on The Strain Aging of Low-Carbon Steels

by W. C. Leslie and R. L. Rickett

The influence of deoxidation practice, prior thermal history, and aging time and temperature on the strain-aging behavior of low-carbon open-hearth steels was investigated. The criterion of aging employed was the increase in yield strength in the tensile test, after straining and aging. Composition, prior heat treatment, and aging conditions were all found to be important in governing the strain-aging characteristics of these steels.

THAT deoxidation changes the strain-aging propensities of low-carbon steels has been known for a long time, but there has been little agreement, and even contradiction, between results obtained by different investigators and between results obtained in the laboratory and in the mill. This investigation was begun in the hope that some of the uncertainties connected with the strain aging of commercial steels could be eliminated.

In considering this problem, it was necessary to define strain aging and to examine the methods used to measure this property. Strain aging can be defined as the changes in properties of a metal or alloy with time, after cold working. The rate at which these changes occur increases as the temperature is raised above atmospheric. The requisite plastic strain is the principal distinction between strain aging and quench aging, the latter being due to precipitation from supersaturated solid solution. Strain aging is also characterized by rapid attainment of maximum hardness at high aging temperatures and lack of softening (overaging) at low aging temperatures.

Several possible criteria of strain aging have been listed by Sachs[1] and by Davenport and Bain.[2] Because changes in mechanical properties are the most easily measured and the most commonly used, consideration of methods to be used in this investigation was confined to three tests: tensile, notch-impact, and hardness. Hardness tests are the most economical and easiest to perform, but produce only one measure of strain aging. Also, as pointed out by Felmly, Hartbower, and Pellini,[3] hardness changes due to aging are not pronounced for steels containing more than 0.15 pct C. Notch-impact tests require careful preparation of large numbers of specimens. Above and below the transition temperature the test lacks sensitivity; furthermore, it is extremely difficult to impart a uniform strain to the specimens, followed quickly by aging and final testing; machining must generally take place after straining.

For these reasons, the tensile test was selected for use. Although this test requires a considerable expenditure of time, labor, and money in preparation of the specimens and performance of the test, more information can be gained than from any other single mechanical test, information which includes upper and lower yield points, yield-point elongation, tensile strength, strain-hardening exponent, reduction of area, and elongation. Low and Gensamer[4] and Schwartzbart and Low[5] also used the tensile test, taking the increase in flow stress after straining in tension and aging as a measure of strain aging. In our work, as in theirs, each specimen was strained an arbitrary amount, sufficient to pass through the

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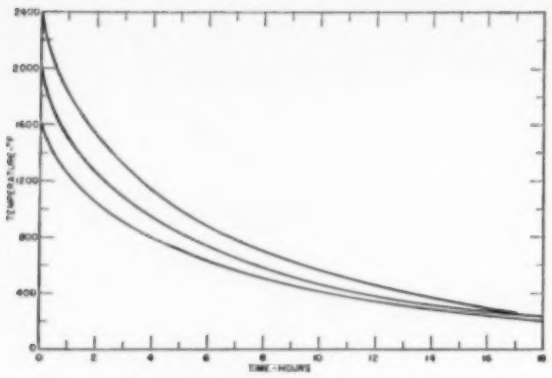

Fig. 1—Typical furnace cooling curves.

yield-point elongation and into the region of uniform plastic strain, then the load was removed and the specimen was given the appropriate aging treatment. The amount by which the yield strength was raised upon reloading was used as a measure of the amount of strain aging.

In using this method, the effect of relaxation must be considered, because this process may go on concurrently with strain aging. No method is known for separating the two phenomena. Low and Gensamer[4] attempted to correct for the effect of relaxation by comparing the strain aging of a steel strained various amounts with the decrease in yield strength (relaxation) of the same steel given identical straining and aging treatments after annealing in wet hydrogen to eliminate strain aging. This method is open to the objection that the relaxation of steel containing carbon and nitrogen may not be the same as the relaxation of steel from which carbon and nitrogen have been removed by annealing in wet hydrogen. Low and Gensamer encountered no relaxation in steel treated in wet hydrogen, then strained 5.1 pct and aged 3 hr at 200°C (390°F). In the present investigation the amount of strain was generally less, the aging times were shorter, and the aging temperatures were lower; it is believed, therefore, that if any relaxation occurred the amount was insignificant.

Materials and Experimental Procedures

With two exceptions, the steels from which specimens were cut came from two basic open-hearth heats, each with graded aluminum additions. One heat was made to rimming practice, then deoxidized by various aluminum additions to the molds. The other heat was killed with ferrosilicon in the furnace, then the same aluminum additions were made to the molds as in the case of the first heat. Identification and composition of all steels used are given in Table I.

Bars from the middle cut of the ingots were forged to 1-in. diameter. These bars were later forged to ⅝-in. diameter, then cut into 4½ in. lengths. Oversize tensile test blanks machined from these short lengths were heat-treated, then finish machined. In an attempt to insure only tensile stresses in the 2-in. gage length, the 0.252-in. diameter reduced section was made 3¼ in. long. The diameter, between the ⅛-in. fillets, was held to 0.2520 ±0.0005 in., with no taper.

All specimens were heat-treated. The specimen blanks were austenitized in a closed-end porcelain tube containing a small amount of carburizing compound. The furnace was brought to temperature, then the specimens were inserted. They were held for 5 min after a thermocouple, which was in a protection tube that touched the specimens, reached the desired temperature. When specimens were to be furnace-cooled or cooled at slower controlled rates, several were treated simultaneously, otherwise they were treated in duplicate. Since cooling rates were found to be of considerable importance, typical furnace cooling curves are presented in Fig. 1. Fig. 2 shows heating and cooling curves determined on two tensile test blanks austenitized at 1600°F, then air-cooled. Chromel-alumel couples (14 gage) were spot welded into center holes ¼ in. deep drilled in the ends of these specimens. Temperatures were followed by means of a high-speed recording potentiometer. When specimens were held isothermally after austenitizing, they were quenched into the largest lead bath available in order that the comparatively large specimens would have the minimum effect on the temperature of the bath.

Tensile tests were performed on a Baldwin-Southwark machine. The specimens, after heat treatment and final machining, were strained 4 pct, or through the yield point elongation, whichever was greater. The maximum extension used on any specimen was 5 pct, with three exceptions which ranged up to 10 pct. The specimens were then unloaded, the wedge-type extensometer was removed,

Table I. Description of Steels

Steel	Deoxidation Practice	Chemical Analysis, Pct								Spectrographic Analysis, Pct					
		C	Mn	P	S	Si	Al+	Al_2O_3	N**	Cr	V	Ti	Mo	Zr	B
A	No Al added	0.10	0.41	0.011	0.024	0.01	0.001	0.001	0.004	0.03	N.D.*	N.D.*	0.02	N.D.*	N.D.*
D	1 lb Al per ton in mold	0.10	0.42	0.011	0.025	0.01	0.013	0.017	0.004						
E	2 lb Al per ton in mold	0.10	0.43	0.010	0.025	0.01	0.047	0.019	0.004	0.03	N.D.	N.D.	0.02	N.D.	N.D.
F	4 lb Al per ton in mold	0.10	0.44	0.012	0.023	0.01	0.144	0.015	0.004						
G	FeSi in furnace, no Al	0.20	0.83	0.011	0.018	0.18	0.004	0.001	0.007	0.03	N.D.	N.D.	0.004	N.D.	N.D.
J	FeSi in furnace, 1 lb Al per ton in mold	0.19	0.82	0.010	0.019	0.16	0.029	0.013	0.006						
K	FeSi in furnace, 2 lb Al per ton in mold	0.19	0.81	0.012	0.019	0.16	0.076	0.016	0.005	0.03	N.D.	N.D.	0.004	N.D.	N.D.
L	FeSi in furnace, 4 lb Al per ton in mold	0.19	0.81	0.011	0.020	0.17	0.158	0.016	0.006						
M	1.9 lb Al per ton in ladle	0.19	0.81	0.014	0.018	0.036	0.035	0.004	0.005	0.03	N.D.	N.D.	0.004	N.D.	N.D.
X	FeSi in furnace	0.25	0.50	0.013	0.027	0.23	0.005	—	0.006						

* V — N.D. — Less than 0.002 pct, if any.
Ti — N.D. — Less than 0.001 pct, if any.
Zr — N.D. — Less than 0.006 pct, if any.
B — N.D. — Less than 0.0005 pct, if any.
\+ — Acid-soluble aluminum.

** Total (acid soluble) nitrogen.

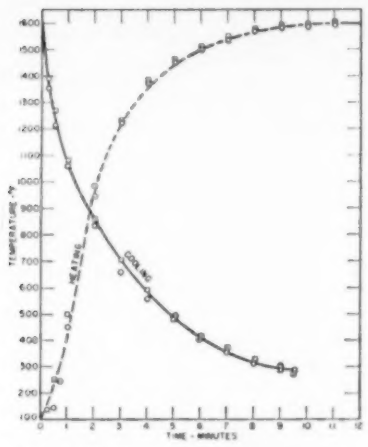

Fig. 2—Heating and cooling curves for tensile test blanks austenitized at 1600°F, then air cooled.

and the specimens were given the desired elevated-temperature aging treatment. At the end of the proper period, they were rapidly cooled by dipping into water at room temperature, dried, and replaced in the grips; the extensometer was replaced in the original gage marks and the test was continued. The time between initial and final straining of the specimens, aside from the time taken up by the aging treatment, was held to a minimum and actually varied between 2 and 7 min. Efforts were made to keep a constant strain rate, as measured between the gage points; it generally ranged between 0.020 and 0.030 in. per in. per min. An autographic load-elongation record was obtained from each specimen, using a 40X magnification and a 6000-lb load range on a 10-in. chart. Values for the upper and lower yield points, load at 4 pct elongation, upper and lower yield points after aging (if any), maximum load, and load at fracture were taken from the load indicating dial of the testing machine. The lower yield point was taken as the lowest value of stress reached during the yield-point elongation. These values were checked against those indicated on the load-elongation record. From this record, values were obtained for initial yield-point elongation and for yield-point elongation after aging. Since there was no taper within the gage length, specimens often broke at, or outside, the gage marks and their elongation could not be measured. Elongation, expressed as percent in 2 in., of specimens that broke

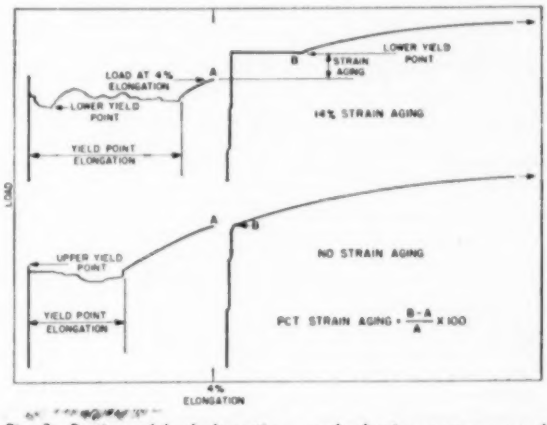

Fig. 3—Portions of load-elongation records showing occurrence and absence of strain aging.

within the gage length was recorded and reduction of area was measured on all specimens in the usual manner. Because of the rapidly changing load, load at fracture could only be estimated.

The extent of strain aging was determined by subtracting the stress at the point *A* (Fig. 3) at which the load was released (generally 4 pct elongation), from *B*, the lower yield point after aging,

Table II. Strain Aging of Specimens of Steels A and E Austenitized at 2000°F, Held Isothermally at 1650°F, Then Air Cooled

Time at 1650°F	Aging Treatment	Col. X: Load at 4 Pct Strain Psi x 10^{-3}		Col. Y: Lower Yield Point After Aging, Psi x 10^{-3}		Y-X: Psi		(100) (Y-X)/X: Pct Strain Aging	
		A	*E*	*A*	*E*	*A*	*E*	*A*	*E*
30 sec	4 hr, 300°F	54.2*	41.4	61.8	48.6	7600	7200	14	17
2 min	4 hr, 300°F	45.3	41.5	52.2	47.9	6900	6400	15	15
5 min	4 hr, 300°F	45.6	41.5	52.9	48.8	7300	7300	16	18
10 min	4 hr, 300°F	45.4	40.8	52.8	46.8	7400	6000	16	15
1 hr	4 hr, 300°F	45.6	42.0†	53.6	48.2	8000	6200	17	15
2 hr	4 hr, 300°F	46.4	40.1	54.0	45.9	7600	5800	16	15
30 sec	15 min, 300°F	45.5	41.3	52.3	47.4	6800	6100	15	15
2 min	15 min, 300°F	45.3	41.9	52.0	48.2	6700	6300	15	15
5 min	15 min, 300°F	45.6	41.1	52.8	47.1	7200	6000	16	15
10 min	15 min, 300°F	45.0	41.4	51.8	47.9	6800	6500	15	16
1 hr	15 min, 300°F	46.1	40.8	53.0	46.4	6900	5600	15	14
2 hr	15 min, 300°F	44.7	39.6	51.8	45.3	7100	5700	16	14
30 sec	1 min, 300°F	45.5	40.9	52.2	46.6	6700	5700	15	14
2 min	5 min, 200°F	45.8	41.4	50.9	46.5	5100	5100	11	12
5 min	30 sec, 200°F	44.9	41.6	45.8	42.6	900	1000	2	2
10 min	1 min, 153°F	45.2	40.8	45.9	41.0	700	200	2	1
1 hr	5 min, 153°F	45.6	40.2	47.0	41.4	1400	1200	3	3
2 hr	1 min, 300°F	45.5	40.0	52.3	44.8	6800	4800	15	12

* Strained 10 pct before aging.
† Strained 4.75 pct before aging.

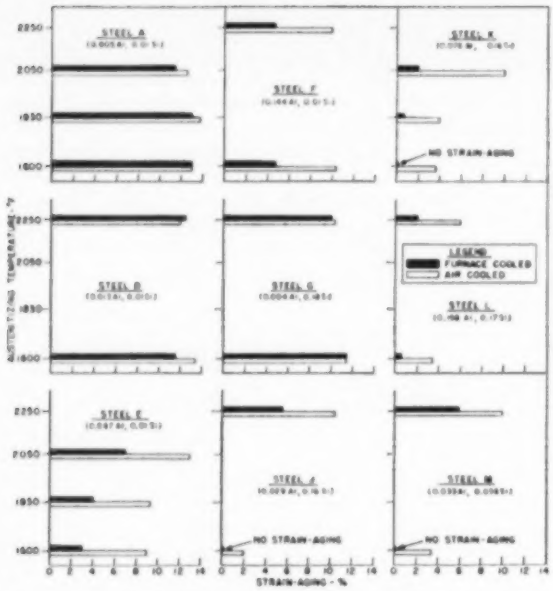

Fig. 4—Effect of austenitizing temperature and cooling rate on subsequent strain aging. Aged 5 min at 210°F.

dividing by A and expressing the result as a percentage, thus, after Schwartzbart and Low,[6]

$$\text{Percent strain aging} = \frac{B-A}{A} \times 100$$

Fig. 3 is a representation of load-elongation diagrams illustrating an example in which aging occurred and one in which it did not occur, with the points of interest marked. The amount of strain aging varied between 0 and 20 pct. A range of ±1 pct strain aging is probably about the limit of accuracy of this method.

A majority of the specimens was aged in boiling water. Those aged 1 min at 300°F and various periods at 200° and 153°F were held in a polyalkylene glycol bath.* The remainder was aged in air in a tempering furnace. Temperature variation in this furnace was held to about ±4°F.

* "Ucon" grade 50-HB-280-X.

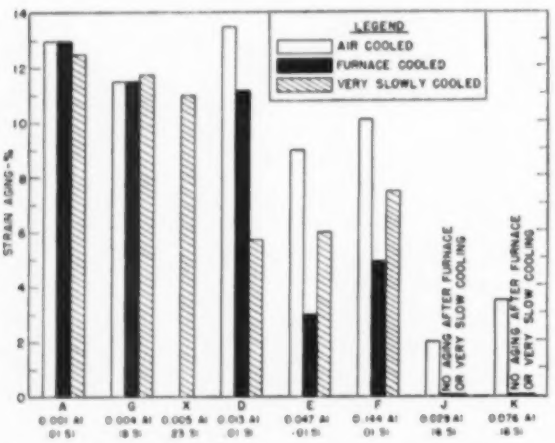

Fig. 5—Effect of rate of cooling from 1600°F on subsequent strain aging. Aged 5 min at 210°F.

Initial Tests: The specimens of the first group tested were austenitized at 2000°F, quenched into lead at 1650°F, held for from 30 sec to 2 hr and air-cooled. This procedure was adopted because of a desire to determine the effects of solution and subsequent precipitation of aluminum nitride on strain aging. Later on, better information on the "solution temperature"[3] and time-temperature requirements for precipitation of aluminum nitride[5] became available and the heat treatments were changed accordingly. Work was confined to two steels, A (rimmed) and E (aluminum-killed). Specimens were tensile tested in the base condition (unaged), also as-aged from 1 min at 153°F to 4 hr at 300°F. The results are presented in Table II.

In the range from 1 to 15 pct strain aging, there was no apparent difference in the strain-aging behavior of the two steels. The only observed difference between the two steels was the higher stress level of the load-elongation curve of the rimmed steel (A), which was 3000 to 4000 psi higher than that of the aluminum-killed steel (E). Time at 1650°F, when aging conditions were held constant, made no difference in the strain-aging results. Aging apparently reached completion within 1 min at 300°F but required more than 5 min (the longest time used) at 200°F and lower.

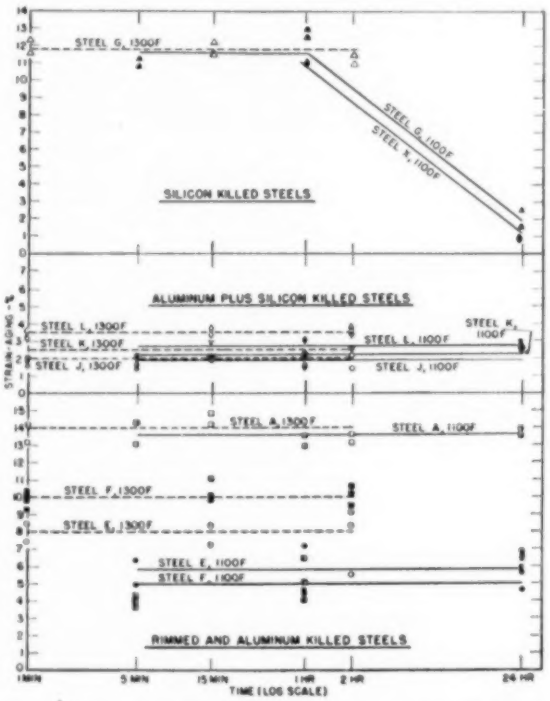

Fig. 6—Effect of time at 1100° and 1300°F on subsequent strain aging. Specimens austenitized at 1600°F.

Variation of Austenitizing Temperature and Cooling Rate: Three steels, A, E, and K, the last containing 0.16 pct Si and 0.076 pct Al, were used in the second phase of the investigation. Since the results of the initial tests indicated no difference in the strain-aging behavior of rimmed and aluminum-killed steels austenitized at 2000°F, held isothermally at 1650°F, and then air-cooled, it was decided to study the effects of varying the austenitizing temperature and the cooling rate from those tem-

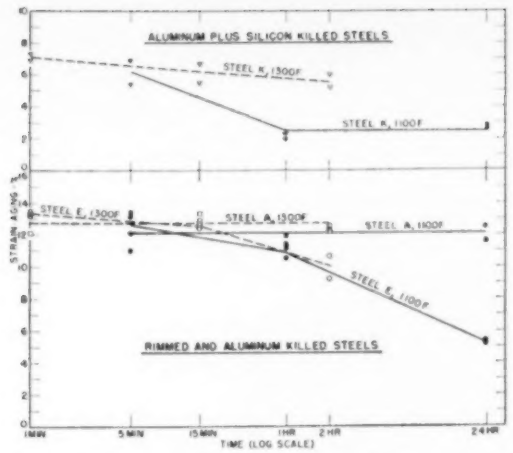

Fig. 7—Effect of time at 1100° and 1300°F on subsequent strain aging. Specimens austenitized at 2050°F.

peratures. The steels were austenitized at 1600°, 1830°, or 2050°F, held 5 min at temperature, then air-cooled, air-cooled and preaged 2 hr in boiling water, or furnace-cooled. The calculated "AlN solution temperature" of steel K containing the highest concentration of aluminum is about 2050°F,[4] and for steel E, about 1920°F. The preaging treatment was performed to determine whether quench aging would interfere with the strain-aging measurements. If the steel is susceptible to quench aging, 2 hr in boiling water is sufficient to cause maximum quench aging and perhaps some overaging,[2] and the effects of quench aging can be separated from those produced by subsequent strain aging. All specimens were aged 5 min in boiling water, after straining. These and all subsequent tests were performed in duplicate, at least.

Some results of this phase of the investigation are included in Figs. 4 and 5. These results indicate that high austenitizing temperatures and rapid cooling rates tend to increase the strain aging of killed steels, and low austenitizing temperatures and slow cooling rates tend to decrease strain aging of these steels. The strain aging of rimmed steel, however, is not affected by austenitizing temperature or cooling rate. Steel K, killed with silicon and aluminum, strain-aged less than steel E, killed with aluminum alone. The preaging treatment had no effect on the amount of strain aging, so this procedure was abandoned.

This work was then extended to include six more steels, D, F, G, J, L, and M (see Table I). Steel L contained the largest amount of aluminum, 0.158 pct, and 0.006 pct N; the calculated "AlN solution temperature" of this steel is about 2220°F, so an austenitizing temperature of 2250°F was used for this series rather than 2050°F. Specimens were air and furnace-cooled from 2250° and 1600°F. Results for this series are also presented in Figs. 4 and 5. Steel G, killed with silicon, was not affected by either the austenitizing temperature or cooling rate. The strain aging of this steel was equivalent to that of the rimmed steel, A. Use of aluminum alone as a deoxidizing agent reduces strain aging, particularly after furnace cooling, but strain aging is not completely eliminated (for aging 5 min in boiling water) even in a steel (F) containing 0.144 pct acid-soluble aluminum. Strain aging was eliminated in steels J, K, L, and M, deoxidized with silicon plus aluminum, by austenitizing at 1600°F followed by furnace cooling. Steel M, containing 0.035 pct Al and 0.036 pct Si, showed no strain aging after furnace cooling from 1600°F, while steel F, containing 0.144 pct Al and 0.01 pct Si, strain-aged about 5 pct.

Effect of Very Slow Cooling: These results led to a determination of the effect of slow, controlled cooling from the austenitizing temperature. Eight steels were used, A, D, E, F, G, J, K, and X. They were cooled at either 13° or 15°F per hr from 1600°F. After heat treatment, the specimens were finish machined, strained 4 pct in tension, then aged 5 min in boiling water. Results are presented in Fig. 5. The strain aging of only one steel, D, was decreased from the strain aging obtained after furnace cooling from 1600°F. Results obtained fall into three groups; the rimmed steel, A, and the two silicon-killed steels G and X strain-aged from 11 to 12 pct, the three aluminum-killed steels, D, E, and F, from 5½ to 7½ pct, and the two silicon-aluminum-killed steels, J and K, did not strain age.

Isothermal Treatments: When steels killed with aluminum or silicon and aluminum are cooled slowly, some change occurs which decreases subsequent strain aging. It was believed, therefore, that the behavior of specimens quenched from the austenitizing temperature to a lower temperature and held isothermally, then air cooled, strained, and aged, might yield information which would aid in the identification of this process. Accordingly, specimens were austenitized at 1600°, 2050°, or 2250°F for 5 min, then quenched into lead at 1100° or 1300°F and held for the following periods: at 1100°F—5 min, 1 hr, or 24 hr, at 1300°F—1 min, 15 min, or 2 hr. Since the process by which strain aging was reduced was believed to be the removal of nitrogen

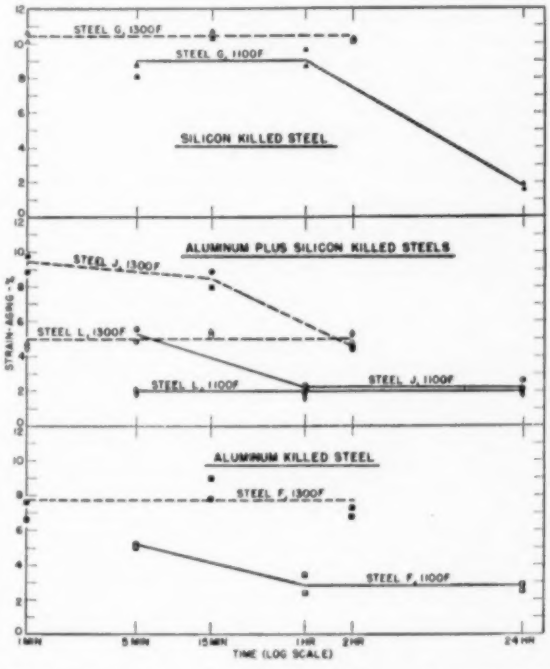

Fig. 8—Effect of time at 1100° and 1300°F on subsequent strain aging. Specimens austenitized at 2250°F.

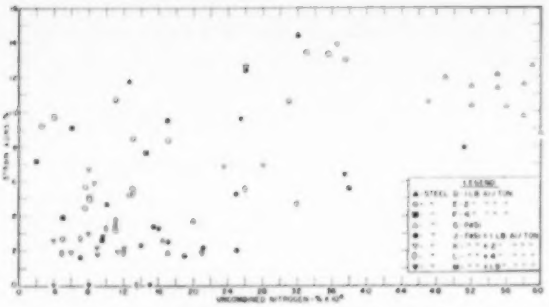

Fig. 9—Correlation between strain aging and uncombined nitrogen in low carbon steels.

from solid solution in ferrite as a result of formation of aluminum nitride, these times were chosen after consideration of the approximate time-temperature relations for complete formation of aluminum nitride in a low carbon steel.[7] The austenitizing temperatures were the same as used in the study of the effect of continuous cooling.

Results are presented in Figs. 6 to 8 in which the percentage of strain aging is plotted against time at the isothermal holding temperature. An unexpected result is illustrated in Figs. 6 and 8. The strain aging of steel G (0.18 pct Si, 0.004 pct Al) had been found to be the same regardless of austenitizing temperature or cooling rate over the range investigated (see Figs. 4 and 5), from which it might be concluded that the strain aging of silicon-killed steels is not influenced by prior heat treatment; however, this conclusion would be incorrect. Although, as shown in Fig. 6, specimens austenitized at 1600°F, then held at 1100°F for 5 min or 1 hr, strain aged about 12 pct, after 24 hr at 1100°F the strain aging was reduced to about 2 pct. However, steel G displayed no change in strain aging after austenitizing at 1600°F, followed by holding at 1300°F for 1 min, 15 min, or 2 hr. The process which reduces strain aging in silicon-killed steels, presumably the formation of silicon nitride, proceeds very slowly. This result was checked by use of another steel, X, containing 0.23 pct Si and 0.005 pct Al. As shown in Fig. 6, the strain aging of this steel after 1 hr or 24 hr at 1100°F is identical with that of steel G. Much the same effect was obtained with steel G when the austenitizing temperature was increased to 2250°F, as shown in Fig. 8.

With the exception of the silicon-killed steels, three levels of strain aging are evident in Fig. 6, with the rimmed steel, A, showing the greatest amount, 13 to 15 pct, regardless of heat treatment, followed by the aluminum-killed steels, E and F, which strain aged 8 to 11 pct after isothermal treatment at 1300°F and 4 to 7 pct after holding at 1100°F. The results for steel F may indicate an increase in subsequent strain aging with increasing time at 1100°F. More data are needed before a definite conclusion can be made; pending this, a horizontal line was drawn in Fig. 6. The third level of strain aging included the steels killed with silicon and aluminum, which strain aged about 2 to 4 pct after being held at 1100° or 1300°F.

The strain-aging behavior of some of the same steels austenitized at 2050°F before isothermal treatment at 1100° and 1300°F is illustrated by Fig. 7. For the rimmed steel, A, the subsequent strain aging is again independent of time at 1100° or 1300°F, and the amount of aging is the same as for this steel austenitized at 1600°F. With steels E (aluminum-killed) and K, (silicon-aluminum-killed) the strain-aging behavior when austenitized at 2050°F, then quenched to 1100° or 1300°F, is quite different from the behavior when the austenitizing temperature was 1600°F. The aluminum-killed steel has the same aging characteristics as the rimmed steel when held at 1300°F for 15 min or less, or when held 5 min at 1100°F. With longer holding times at 1100° or 1300°F, the subsequent strain aging is reduced. After quenching from 2050° to 1300°F and holding for 2 hr, the amount of strain aging is slightly greater than when the steel was austenitized at 1600°F, then held 2 hr at 1300°F. When held 24 hr at 1100°F, after austenitizing at 2050°F, the strain aging was the same as after austenitizing at 1600°F and holding 5 min to 24 hr at 1100°F.

The behavior of steel K (silicon-aluminum-killed) is similar in that subsequent strain aging was reduced after austenitizing at 2050°F and quenching to 1100° or 1300°F. An hour at 1100°F was sufficient to bring the amount of strain aging down to the same level (approximately 2 pct) reached when the steel was austenitized at 1600°F and held at 1100° or 1300°F. Two hours at 1300°F after quenching from 2050°F was not sufficient to bring the strain aging down to the level reached when the steel was quenched from 1600° to 1300°F and held 1 min to 2 hr.

The results obtained when killed steels were quenched from 2250°F to 1100° or 1300°F and held at these lower temperatures are illustrated in Fig. 8. Except for steel L, the extent of strain aging decreased with increasing times at 1100°F. Only steel J was affected by increasing the time at 1300°F, within the range investigated.

The subsequent strain aging of killed steels tended to decrease with time at 1100° or 1300°F, until an equilibrium level characteristic of each steel was reached. This level was independent of the austenitizing temperature, but raising the austenitizing temperature increased the time required at the lower temperatures for equilibrium to be reached. In the aluminum-killed or aluminum-silicon-killed steels, 5 min at 1600°F followed by 1 min at 1300°F and air cooling or 5 min at 1100°F and air cooling suffice for the attainment of equilibrium. In steels killed with silicon alone the reaction is very sluggish and 24 hr at 1100°F are required for reduction of strain aging to the equilibrium level. In the case of a rimmed steel, none of the prior heat treatments tested affected strain aging. The isothermal treatments at 1100° or 1300°F did not completely eliminate subsequent strain aging, even in steels killed with aluminum and silicon, although these steels showed no strain aging after furnace cooling from 1600°F. From an examination of Figs. 6 to 8, it appears that strain aging of killed steels is reduced by a process which bears the characteristics of precipitation from solid solution. These results support the conclusion that the strain aging of aluminum-killed or silicon-killed steels is reduced through the removal of nitrogen from solution in ferrite by formation of aluminum or silicon nitrides. Formation of these nitrides in steel is dependent on heat treatment.[6-10] The solubility of these nitrides at 1100°F in the steels used evidently is sufficient to cause about 2 pct strain aging, which is a minor amount;

in order to eliminate the aging it is necessary to cool slowly below this temperature. The effect of raising the austenitizing temperature is to increase the solubility of the nitrides and to increase the time required for their precipitation at lower temperatures.

Determination of Aluminum Nitride: In an attempt to determine directly the influence of nitrogen in solution in ferrite on strain aging, a number of broken tensile test specimens of eight steels were analyzed for "AlN nitrogen" by the Beeghly method.[9] The AlN nitrogen obtained by this procedure was subtracted from the total (acid soluble) nitrogen to give the concentration of nitrogen in solution in ferrite. The Beeghly method suffers from lack of any standards; also, aluminum nitride particles in the very early stages of growth cannot be separated from the ferrite matrix. During the course of the work it was found that the presence of silicon nitride, Si_3N_4, interferes with the determination of AlN nitrogen.[10] Except in steels containing more than about 0.5 pct Si, the total of Si_3N_4 plus AlN nitrogen will be obtained by the Beeghly method. Moreover, it is apparently necessary to determine the uncombined nitrogen to the fourth place to the right of the decimal point in order to measure its effect on strain aging and a method based on chemical separation of a precipitate is hardly likely to give this degree of accuracy. However, since no other method was available, it was decided to use this technique. Results are presented in Fig. 9. The most that can be said, from the evidence shown here, is that uncombined nitrogen must be reduced to a very small concentration before strain aging is eliminated. Fast[12] found that as little as 0.001 pct N caused maximum strain aging in high purity iron and 0.0004 pct N was sufficient to produce an easily measured amount. From his results, it seems that the uncombined nitrogen in low-carbon steels must be reduced to about 0.0001 pct or less to eliminate strain aging.

Variation of Aging Conditions: In most of the experiments described up to this point the specimens were aged 5 min in boiling water. To determine the effect of varying the aging conditions, particularly in the case of steels which could be rendered nonaging as measured after aging 5 min in boiling water, further tests were made on five steels, A, E, F, K, and L. Specimens were furnace-cooled from 1600°F, and in addition specimens of steel K were air-cooled from 2050°F, which is about 25°F above the calculated "AlN solution temperature" for this steel. Duplicate specimens were strained 4 pct, aged 5 min in boiling water (to check previous results), 1 hr in boiling water, 1 hr at 345°F or 1 hr at 480°F. Results are presented in Fig. 10a and b. The strain aging of rimmed steel, A, increased from about 14 pct when aged 5 min in boiling water to 16 or 17 pct when aged 1 hr in boiling water. The aging of this steel then remained constant even when the aging treatment was 1 hr at 480°F. Steel E (0.047 pct Al, 0.01 pct Si) strain aged 3 pct after 5 min in boiling water and about 9 pct after 1 hr at this temperature. It showed an increase to 12 or 13 pct after 1 hr at 480°F. The behavior of steel F (0.144 pct Al, 0.01 pct Si) was quite similar; thus, increasing the aluminum content of the steel from 0.047 to 0.144 pct did not influence the aging behavior. The behavior of steels K (0.76 pct Al, 0.16 pct Si) and L (0.158 pct Al, 0.17 pct Si), furnace-cooled from 1600°F, was identical. They showed no aging after 5 min or 1 hr at 212°F. After 1 hr at 345°F they aged about

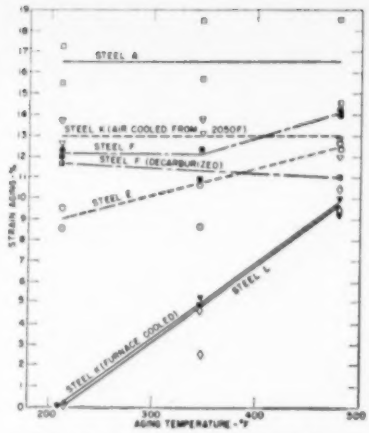

Fig. 10a—Strain aging of steels furnace-cooled from 1600°F (except as noted), strained 4 pct, and aged 1 hr at indicated temperatures.

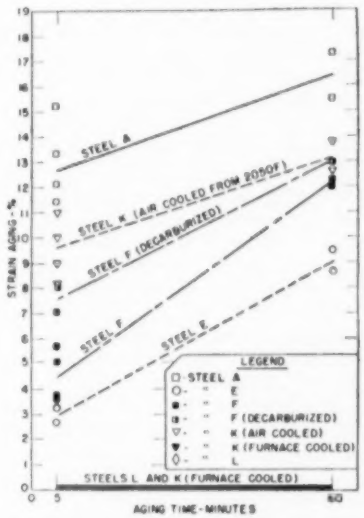

Fig. 10b—Influence of time at 210°F on strain aging of steels furnace-cooled from 1600°F (except as noted), then strained 4 pct, and aged.

5 pct, and about 10 pct after 1 hr at 480°F. Still more aging might have occurred had the aging temperature been higher or the time at 480°F been longer. This may be said also for steels F and E. In the case of steel K, air-cooled from 2050°F, the aging amounted to about 9 pct after 5 min in boiling water and 13 pct after 1 hr in boiling water. It remained constant at about 13 pct after 1 hr at 347°F and 1 hr at 480°F. Thus, a thoroughly killed steel, given different heat treatments, can show 0 or 13 pct strain aging after straining 4 pct and aging 1 hr in boiling water.

The results of these experiments indicate that composition, thermal history prior to straining, and aging conditions are all of importance in determining the strain-aging characteristics of low-carbon steel.

Discussion of Results

Mechanism of Strain Aging: A large amount of evidence[1, 6, 11-14, 25] has accumulated which lends sup-

port to the conclusion that the strain aging of mild steel is due to carbon and nitrogen in solution in ferrite. The mechanism by which these interstitial solute atoms produce the effects of strain aging is not known; the most promising hypothesis is that advanced by Cottrell.[12, 35-37] The region around a dislocation provides more favorable sites for interstitial solute atoms (carbon and nitrogen) than can be found in the undisturbed lattice, so these atoms tend to cluster around dislocations, forming "atmospheres." These atmospheres hinder the movement of the dislocations under applied external loads. When the external force on the dislocations exceeds the maximum force which can be exerted by their atmospheres, the metal exhibits a sharp yield point as the first dislocations break loose from their clouds of solute atoms. These moving dislocations interact with dislocations still anchored by their atmospheres, causing them to break loose, thus producing the yield point elongation. When strained iron is aged, the interstitial solute atoms again diffuse to regions around dislocations. The metal shows a return of the yield point (strain aging) when it is again subjected to external stress.

It is not possible to predict the concentration of solute atoms necessary to produce strain aging, since this will depend upon the number of solute atoms required to anchor a dislocation and also upon the density of dislocations; however, a rough estimate can be made. It was estimated by Seitz and Read[38] that an annealed metal contains 10^8 dislocations per square centimeter and that a heavily cold-worked metal saturated with dislocations will contain 10^{12} dislocations per square centimeter. Annealed iron containing 0.0004 pct N by weight, for example, will have between 100 and 1000 nitrogen atoms per dislocation, which is certainly enough for formation of atmospheres. If this same iron is considered to contain 10^{10} dislocations per square centimeter after slight straining, there will be from 1 to 10 nitrogen atoms per dislocation. If the Cottrell mechanism is the one which operates, it is easy to see why the concentration of interstitial solute atoms must be brought to an extremely low level before strain aging can be eliminated.

As pointed out by Fast,[11] the rate of strain aging will depend upon the product of the solubility and diffusivity of the interstitial solute atoms carbon and nitrogen. Fast stated that nitrogen was the essential cause of the strain aging of iron at room temperature or slightly above because of its greater solubility in α iron in this temperature range as compared with carbon. Since the publication of his paper, more data on the diffusivity and solubility of carbon and nitrogen in α iron have become available. For the diffusivity of carbon in α iron between −35° and 700°C (−31° and 1292°F) Wert[39] gives the equation

$$D_C = 0.02e^{-\frac{20,100}{RT}}$$

This is only slightly different from that given by Stanley,[20] whose work was confined to temperatures above 514°C (957°F),

$$D_C = 0.0079e^{-\frac{18,100}{RT}}$$

The diffusivity of nitrogen in α iron, as given by Wert,[21] is less certain, since determinations were made only between −30° and 40°C (−22° to 104°F) and since there is no other work against which the equation can be checked.

$$D_N = 0.003e^{-\frac{18,200}{RT}}$$

When the diffusivities of carbon and nitrogen at 100°C are calculated by these equations the following results are obtained:

$$D_C = 3\text{x}10^{-16} \text{ sq cm per sec (Wert)}$$

$$D_C = 20\text{x}10^{-16} \text{ sq cm per sec (Stanley)}$$

$$D_N = 7\text{x}10^{-16} \text{ sq cm per sec}$$

The diffusivities of carbon and nitrogen in α iron at 100°C (212°F) appear to be nearly equal.

For the solid solubility of carbon in α iron between 150° and 700°C (302° and 1292°F) Wert[39] gives the equation

$$C_C = 2.55e^{-\frac{9,700}{RT}}$$

This is in agreement with the results of Stanley,[20] Smith,[23] and Dijkstra.[24] In the case of nitrogen, the available data are not as reliable. From the work of Dijkstra,[24] in the temperature range 200° to 590°C (392° to 1094°F) Fast[11] gives the equation

$$C_N \text{ (log \% N)} = -\frac{7100}{4.575\,T} + 0.70$$

The solubilities at various temperatures calculated from these two equations are given in Table III. Thus, from an examination of the best data available, it seems likely that the greater effectiveness of nitrogen in producing strain aging as compared with carbon is due to its greater solubility. At low temperatures, the solubility of nitrogen in α iron is about 100 times that of carbon.

Table III. Solubilities of Carbon and Nitrogen

Temperature	Solubility of Carbon, Wt Pct	Solubility of Nitrogen, Wt Pct
20°C (68°F)	0.15x10^{-6}	25x10^{-6}
100°C (212°F)	5.4 x10^{-6}	350x10^{-6}
207°C (405°F)	100 x10^{-6}	3000x10^{-6}
288°C (550°F)	500 x10^{-6}	8700x10^{-6}

Apparently no one has succeeded in producing strain aging in iron at temperatures below 100°C that could definitely be traced to carbon alone. Fast[11] found that 40 hr at 50°C (122°F) produced no strain aging in a specimen of high purity iron to which 0.04 pct C had been added. Only very slight aging (increase in hardness of 3 VPN) was produced by 2 hr at 100°C. If our supposition is correct, a steel in which all the nitrogen is combined as nitrides will strain-age only if raised to a temperature at which the solubility of carbon is sufficient to cause aging. This temperature is probably close to 100°C.

Effect of Aging Conditions: Some of the apparently contradictory results reported in the literature can now be reconciled. Edwards, Jones, and Walters,[28] using commercial rimmed and silicon-killed steels with 0.08 pct C, conducted experiments to determine the effect of cooling rate on aging. They found aging to occur after both air and furnace cooling from 950°C (1742°F), and after air cooling from 950°C, reheating to 600°C (1112°F) and slow cooling. Specimens from a special heat containing 0.48 pct Al aged as much as rimmed steels. The aging treatment was 1 hr at 250° or 300°C (482° or 572°F).

Table IV. Strain Aging of a Decarburized, Aluminum-Killed Steel, Steel F

Specimen	Aging Treatment	A: Load at 4 Pct Strain, Psi x 10^{-3}	B: Lower Yield Point After Aging, Psi x 10^{-3}	B-A, Psi	Pct Strain Aging	Acid Soluble Al, Pct	Total (Acid Soluble) N, Pct	N Combined as AlN, Pct	C, Pct	S, Pct
1	5 min, 210°F	27.6	29.8	2200	8	0.105	0.0070	—	0.0068	
2	5 min, 210°F	27.4	29.4	2000	7	—	0.0078	0.0074	0.0052	0.021
3	1 hr, 210°F	26.8	29.9	3100	12	—	0.0075	0.0067	0.0046	0.022
4	1 hr, 480°F	27.5	30.4	2900	11	—	0.0097	0.0085	0.0073	0.021

Edwards, Phillips, and Jones,[27] using a series of low-carbon steels containing from 0.02 to 3.39 pct Al, air-cooled and furnace-cooled from 950° and 1050°C (1742° and 1922°F), found these alloys to age after straining 6 pct in tension and aging 1 hr at 250°C (482°F). These results were puzzling in view of the fact that "nonaging" aluminum-killed steels were being produced commercially. The strain aging produced was almost certainly due to the relatively high aging temperature used. As shown in Fig. 10 of this paper steels thoroughly killed with silicon and aluminum that show no sign of strain-aging after being strained 4 pct and held 1 hr at 212°F, age much more when strained 4 pct and held 1 hr at 480°F. Presumably, the nitrogen in these steels was combined as aluminum or silicon nitride by furnace cooling from 1600°F, but the carbon was still free to cause strain aging if the aging temperature was sufficiently high. The effect is not likely to be due simply to changes in rate of aging, for the silicon-aluminum-killed steels showed no change in aging with variations in aging time (up to 1 hr) at 212°F.

Effectiveness of Deoxidizing Elements: One result of the present work which is difficult to rationalize on the basis of decrease of aging by combination of the nitrogen is the greater effectiveness of deoxidation with aluminum and silicon as compared with deoxidation by aluminum alone. As shown by Figs. 4 and 5, steels containing only 0.01 pct Si and from 0.013 to 0.144 pct Al strain-aged from 3 to 7 pct, even after furnace cooling or very slow cooling from 1600°F. Steels containing 0.036 pct Si and 0.035 pct Al or 0.16 pct Si with 0.029 to 0.158 pct Al showed no aging after furnace cooling or very slow cooling from 1600°F. Aging conditions were constant at 5 min in boiling water. If elimination of aging under these conditions is due to removal of nitrogen from solution by combination with the deoxidizing elements, it is difficult to see why strain aging was not eliminated in the steel containing 0.01 pct Si, 0.144 pct Al, and 0.004 pct N by formation of aluminum nitride. Very slow cooling from 1600°F favors complete formation of AlN.[7] By use of the data of Darken, Smith, and Filer[4] the solubility product of aluminum nitride, i.e., the product of the concentrations of aluminum and nitrogen in solution, can be calculated for any temperature in the austenitic range. The solubility product of aluminum nitride in ferrite can only be approximated. The ratio between the solubility product in ferrite and the solubility product in austenite will equal the ratio between the concentrations of nitrogen and aluminum in solution in ferrite and in austenite at equilibrium, or,

$$\frac{K_s(\alpha)}{K_s(\gamma)} = \frac{C_N(\alpha)\, C_{Al}(\alpha)}{C_N(\gamma)\, C_{Al}(\gamma)}$$

Reliable data for the nitrogen concentrations were furnished by Darken, but the situation is not as satisfactory in the case of aluminum. The partition of aluminum between ferrite and austenite at equilibrium is not known,[28] but the ratio cannot be far from one. At 1400°F (760°C) the solubility product of aluminum nitride in ferrite for a steel containing 0.144 pct Al and 0.004 pct N will be, approximately,

$$\frac{K_s(\alpha)}{8\times10^{-4}} = \frac{0.0022}{0.028} \times 1$$

$$K_s(\alpha) = 8\times10^{-5}$$

This is the product of the concentrations of aluminum and nitrogen, so there will be about 6×10^{-4} pct N in solution in the ferrite. Since the solubility of nitrogen in ferrite decreases with temperature, the concentration of nitrogen in solution at 212°F will be even smaller than this extremely low figure and much less than required to produce strain aging. Nevertheless, when this steel was cooled at about 13°F per hr from 1600°F to allow equilibrium to be approached, then strained 4 pct and aged 5 min at 212°F, it strain aged 6 to 9 pct. A steel containing 0.029 pct Al, 0.16 pct Si, and 0.006 pct N, given the same treatment, showed no strain aging. An explanation of this behavior and of the greater effectiveness of deoxidation with aluminum and silicon as compared with deoxidation by aluminum alone may be that the aluminum cannot react with the nitrogen because of prior combination with some other element. This other element is almost certainly not oxygen; the Al_2O_3 content of the aluminum-killed steel is 0.015 pct and the "acid soluble" aluminum content is 0.144 pct. There is a possibility that aluminum was combined with sulphur and perhaps with carbon. Iron-aluminum carbides have been reported.[29, 30] This hypothesis might be tested by examining the strain-aging behavior of an aluminum-killed steel from which carbon and sulphur had been removed but not nitrogen. Accordingly, four tensile test blanks of steel F (0.144 pct Al) were held in a flowing 94 pct H_2-6 pct N_2 atmosphere at 2280°F for from 48 to 50 hr. The gas mixture was bubbled through water at room temperature before entering the furnace. The specimens were rapidly cooled to room temperature, placed in a furnace at 1600°F, held for 10 min, then cooled in the furnace to room temperature. After final machining the specimens were strained 4 pct, aged, and pulled to fracture. The broken specimens were then analyzed for aluminum, nitrogen, carbon, and sulphur. Results of the aging tests and analyses are shown in Table IV. The nitrogen content of the steel was close to the expected value, but the carbon content was greater than anticipated. The sulphur content remained unchanged. Removal of nearly all of the carbon from this steel did not alter its strain-aging characteristics (Fig. 10). The apparent reluctance of aluminum, even when present in consider-

able excess, to combine with the last traces of nitrogen probably is not due to prior combination with carbon and the sulphur present is sufficient to combine with less than a fifth of the aluminum. The cause of the slight strain aging of slowly cooled aluminum-killed steels remains a mystery.

Apparently, the function of silicon in a silicon-aluminum-killed steel is to combine with the last traces of nitrogen which are not removed by combination with aluminum. Deoxidation with silicon alone is not an efficient method for eliminating strain aging because of the very slow formation of silicon nitride, see Figs. 6 and 8.

Correlation with Previous Work

The conclusions reached in this study have sometimes been implied by other investigators, though seldom stated explicitly. Hayes and Griffis[21] were aware of the importance of heat treatment in the production of "nonaging" steels. Their heat treatment consisted of heating below the A_{c_3} preferably below the A_{c_1}, then slow cooling. Our evidence confirms the necessity for slow cooling, but does not confirm the need for the top heating temperature to be below the A_{c_3}.

Altenburger[22] stated many of the same conclusions reached in this paper. He believed the strain aging of mild steel to be due to nitrogen, and that nitrogen may be fixed by silicon, aluminum, zirconium, titanium, or vanadium. He also stated that the susceptibility of killed steels to strain aging depends upon their prior history, and that estimates of aging susceptibility in the hot-rolled condition are unreliable because of the great variation in cooling rates. The criterion of strain aging used in Altenburger's work was the difference in tensile strength of sheet specimens tested at 75° and 400°F. Annealing temperatures of 1150° or 1200°F seemed to be more favorable for reducing the strain aging of silicon-killed sheet than 1050° or 1300°F. Altenburger states that although silicon can be used to produce "nonaging" sheet, it is not used because of its hardening effect.

The effects on Charpy impact strength at room temperature produced by normalizing aluminum-killed and rimmed open-hearth steels at 1650°F in contrast to furnace cooling from 1650°F, each followed by straining and aging at temperatures ranging from 300° to 660°F, are presented by Enlund.[23] Both rimmed and killed steels remained ductile at room temperature after the normalizing treatment, but the rimmed steel was embrittled at room temperature after slow cooling while the aluminum-killed steel remained ductile. A determination of the shift in transition temperatures due to aging would have been more illuminating, but these results do illustrate the danger of comparing results obtained by use of different criteria of strain aging. Enlund concluded that aging properties of a steel are governed by the composition, prior heat treatment, and microstructure; slow cooling was detrimental to impact strength after aging. This author recommended that a quench-and-temper treatment be given to mild steels to prevent brittleness due to aging. The change in stress required to cause plastic flow, as used in the present investigation, is more suitable for determination of changes occurring within ferrite than is the impact test, which is very sensitive to changes in ferrite grain size and carbide distribution. Prior heat treatment may influence formation of nitrides, ferrite grain size, and carbide distribution, but in Enlund's work, effects produced by combination of nitrogen may have been completely masked by gross microstructural changes.

Good qualitative correspondence between strain-aging effects as measured by the tensile test and the Charpy notch-impact test were reported by Felmley, Hartbower, and Pellini.[3] These investigators used four steels; rimmed, silicon-killed, aluminum-silicon-killed, and titanium-vanadium-silicon-killed. Specimens were normalized at 1650°F, then reheated to 1200°F and either furnace-cooled or brine-quenched. Only the rimmed and silicon-killed steels strain aged when furnace cooled from 1200°F, as indicated by the tensile test data, and only these two steels showed marked increases in transition temperature. When the steels were brine quenched from 1200°F, all four showed pronounced strain aging by both the tensile and impact criteria. These results are in general agreement with results of this investigation. The experimental procedures of Felmley, et al., were less likely to produce large changes in microstructure, so their results are more nearly a measure of the strain-aging effects than are those of Enlund, who necessarily measured the effect of gross changes in the microstructure on the impact properties, as well as strain-aging effects.

Daniloff, Mehl, and Herty,[24] using impact data obtained on normalized steels, concluded that the more thorough the deoxidation of the steel, the less was the tendency to strain age.

Comstock and Lewis[25] reported that strain-aging embrittlement can be prevented by titanium deoxidation as well as by aluminum deoxidation, and that susceptibility to strain aging depended, in part, upon prior heat treatment.

Summary and Conclusions

The effect of composition, heat treatment, and aging conditions on strain aging were determined, using specimens taken from two low-carbon open-hearth heats, one of which was silicon-killed, the other made to rimming practice. A graded series of aluminum additions was made to ingots of both heats (Table I). Tensile test specimens from bars rolled from these ingots were heat-treated, machined, strained 4 pct, or through the yield point elongation, whichever was greater, then aged and pulled to fracture. The extent of strain aging was measured by the increase in yield strength after aging and expressed in percent. The conclusions reached are based upon use of this criterion and caution should be exercised in predicting results to be expected by use of other measures of strain aging, such as behavior in the notch-impact test. The results obtained are in agreement with those reported in recent investigations.

The conclusions are as follows:

1—Strain aging of commercial steels is primarily due to nitrogen in solution in ferrite; deoxidation with silicon and aluminum affects strain aging principally through formation of nitrides and removal of nitrogen from solution in ferrite. Carbon is a secondary cause of strain aging and for this reason, aluminum or silicon-killed steels cannot be completely "nonaging" under all conditions. When high aging temperatures are used, carbon will cause strain aging even in steels completely killed with aluminum and silicon. To produce a steel which will show no strain-aging effects would require the addition of elements which reduce the solubility of both carbon and nitrogen in ferrite to a very low level.

2—The strain aging of killed steels is governed by prior heat treatment. The heat treatments which reduce subsequent strain aging are those which promote complete precipitation of nitrides. For aluminum-killed or aluminum-silicon-killed steels, slow cooling from the hot rolling temperature is effective. For silicon-killed steels, extended treatment in the neighborhood of 1100°F is required, preferably followed by slow cooling. Conversely, killed steels can be made susceptible to strain aging by rapid cooling, which retains nitrogen and carbon in solution in ferrite. The usual types of rimmed steel strain age regardless of heat treatment because they do not contain elements which form stable carbides and nitrides.

3—To reduce strain aging of commercial steels to a low level, it is necessary to reduce nitrogen in solution in ferrite to a very low concentration, in the neighborhood of 0.0001 pct.

4—Nitrogen is more effective than carbon in producing strain aging because of its greater solubility in ferrite at low temperatures. When solubility of carbon in ferrite is increased by high aging temperatures, strain aging is produced even when nitrogen has been completely removed from solution.

5—Strain aging may be reduced by deoxidation with either aluminum or silicon, followed by the proper heat treatment. Because of the more rapid formation of aluminum nitride (AlN) and its greater range of stability as compared with silicon nitride (Si_3N_4), deoxidation with aluminum is more effective than deoxidation with silicon. For reasons which are not entirely clear, deoxidation with silicon and aluminum is much more effective in preventing strain aging than deoxidation with either alone.

Acknowledgments

The authors wish to thank W. B. Seens and W. L. Jensen for their aid in conducting the tensile tests. Chemical analyses were performed by G. W. Momeyer and Mrs. Irene Christmas. Spectrographic analyses were done at Gary Steel Works. We are indebted to several members of the staff for helpful suggestions and discussion, in particular, to G. V. Smith, F. Garofalo, and L. S. Darken.

References

[1] G. Sachs: Strain Aging Criteria. *Iron Age* (May 13, 1948) **161**, p. 79.

[2] E. S. Davenport and E. C. Bain: The Aging of Steel. *Trans.* ASM (1935) **23**, p. 1047.

[3] C. R. Felmley, C. E. Hartbower, and W. S. Pellini: Effect of Cooling Rate on the Aging Characteristics of Structural Steels. Advance Copy, A.W.S. (1951).

[4] J. R. Low, Jr. and M. Gensamer: Aging and the Yield Point in Steel. *Trans.* AIME (1944) **158**, p. 207.

[5] H. Schwartzbart and J. R. Low, Jr.: The Yielding and Strain-Aging of Carburized and Nitrided Single Crystals of Iron. *Trans.* AIME (1949) **185**, p. 637; JOURNAL OF METALS (September 1949).

[6] L. S. Darken, R. P. Smith, and E. W. Filer: Solubility of Gaseous Nitrogen in Gamma Iron and the Effect of Alloying Constituents—Aluminum Nitride Precipitation. *Trans.* AIME (1951) **191**, p. 1174; JOURNAL OF METALS (December 1951).

[7] W. C. Leslie, R. L. Rickett, C. L. Dotson, and C. S. Walton: Solution and Precipitation of Aluminum Nitride in Relation to the Structure of Aluminum-Killed Low-Carbon Steels. To be published.

[8] W. C. Leslie, K. G. Carroll, and R. M. Fisher: Diffraction Patterns and Crystal Structure of Si_3N_4 and Ge_3N_4. *Trans.* AIME (1952) **194**, p. 204; JOURNAL OF METALS (February 1952).

[9] H. F. Beeghly: Determination of Aluminum Nitride Nitrogen in Steel. *Analytical Chemistry* (1949) **21**, p. 1513.

[10] H. F. Beeghly: Behavior of Nitrogen and some of its Compounds in Steel. *Analytical Chemistry* (1952) **24**, p. 1095.

[11] J. D. Fast: Ageing of Iron and Steel. *Iron and Coal Trades Review* (1950) **160**, p. 837.

[12] A. H. Cottrell and A. T. Churchman: The Change of Electrical Resistance During the Strain Ageing of Iron. *Journal* Iron and Steel Inst. (1949) **162**, p. 271.

[13] S. Harper: Precipitation of C and N in Cold Worked Alpha Iron. *Physical Review* (1951) **83**, p. 708.

[14] A. N. Holden: The Yielding Behavior of Iron Single Crystals. *Journal of Applied Physics* (1951) **22**, p. 1290.

[15] A. H. Cottrell: Effect of Solute Atoms on the Behavior of Dislocations. *Report on Conference on Strength of Solids.* The Physical Society, London (1948).

[16] A. H. Cottrell and B. A. Bilby: Dislocation Theory of Yielding and Strain Ageing of Iron. *Proc.* Phys. Soc., London (1949) **62A**, p. 49.

[17] A. H. Cottrell: The Yield Point in Single Crystal and Polycrystalline Metals. *Symposium on Plastic Deformation of Crystalline Solids.* (May 1950) p. 60. Pittsburgh. Mellon Institute.

[18] F. Seitz and T. A. Read: Theory of the Plastic Properties of Solids. II. *Journal of Applied Physics* (1941) **12**, p. 170.

[19] C. A. Wert: Diffusion Coefficient of Carbon in Alpha Iron. *Physical Review* (1950) Series 2, **79**, p. 601.

[20] J. K. Stanley: The Diffusion and Solubility of Carbon in Alpha Iron. *Trans.* AIME (1949) **185**, p. 752; JOURNAL OF METALS (October 1949).

[21] C. A. Wert: Measurements on the Diffusion of Interstitial Atoms in B.C.C. Lattices. *Journal of Applied Physics* (1950) **21**, p. 1196.

[22] C. A. Wert: Solid Solubility of Cementite in Alpha Iron. *Trans.* AIME (1950) **188**, p. 1243.

[23] R. P. Smith: Equilibrium of Iron-Carbon Alloys with Mixtures of CO/CO_2 and CH_4/H_2. *Journal* ACS (1946) **68**, p. 1163.

[24] L. J. Dijkstra: Precipitation Phenomena in the Solid Solutions of Nitrogen and Carbon in Alpha Iron below the Eutectoid Temperature. *Trans.* AIME (1949) **185**, p. 252; JOURNAL OF METALS (March 1949).

[25] A. H. Cottrell and A. T. Churchman: Discussion on Homogeneous Yielding of Carburized and Nitrided Single Iron Crystals. *Trans.* AIME (1949) **185**, p. 877; JOURNAL OF METALS (November 1949).

[26] C. A. Edwards, H. N. Jones, and B. Walters: A Study of Strain-Age-Hardening of Mild Steel. *Journal* Iron and Steel Inst. (1939) **139**, p. 341.

[27] C. A. Edwards, D. L. Phillips, and H. N. Jones: The Influence of Some Special Elements Upon the Strain-Ageing and Yield Point Characteristics of Low-Carbon Steels. *Journal* Iron and Steel Inst. (1940) **142**, p. 199.

[28] *Metals Handbook.* (1948) p. 1161. Cleveland. ASM.

[29] F. R. Morral: The Constitution of Iron-Rich Fe-Al-C Alloys. *Journal* Iron and Steel Inst. (1934) **130**, p. 419.

[30] K. Löhberg and W. Schmidt: Die Eisenecke des Systems Eisen-Aluminium-Kohlenstoff. *Archiv. Eisenhuttenw.* (1938) **12**, p. 607.

[31] A. Hayes and R. O. Griffis: U. S. Patent 2,069,758 (1937).

[32] C. L. Altenburger: The Metallurgy of Cold Reduced Sheets. *Yearbook* Amer. Iron and Steel Inst. (1947) p. 459.

[33] B. D. Enlund: The Aging of Steel. *Jernkontorets Annaler* (1946) **130**, p. 553; *Engineering Digest* (1947) **4**, p. 61.

[34] B. N. Daniloff, R. F. Mehl, and C. H. Herty, Jr.: The Influence of Deoxidation on the Aging of Mild Steels. *Trans.* ASM (1936) **24**, p. 595.

[35] G. F. Comstock and J. R. Lewis: A Comparison of Aluminum and Titanium Deoxidation for Preventing Strain Aging Embrittlement in Low Carbon Steel. *Trans.* ASM (1945) **34**, p. 425.

Some Properties of Columbium Containing Nitrogen

by Choh-Yi Ang and C. Wert

Quench aging of supersaturated solid solutions of nitrogen in columbium takes place in reasonable times in the temperature range 300° to 500°C. Changes in internal friction, hardness, and electrical resistivity are found to accompany this change.

THERE is practically no detailed information in the literature concerning interstitial solid solutions in either columbium or tantalum. The fact that both of these metals are used extensively commercially in both pure and alloyed states makes studies of their properties of value. While the plan is to study both these metals and their alloys extensively, so far only a small number of measurements have been made. This paper presents data obtained in the initial investigations of columbium.

The principal interstitial impurities of columbium are likely to be hydrogen, carbon, oxygen, and nitrogen. The first of these, hydrogen, is outside the scope of internal friction measurements at present and nothing quantitative is known about the initial hydrogen content of the specimens. However, it is believed that it is completely absent after the preliminary heat treatments are carried out. The carbon content of the original samples is low and can be reduced still further during sample preparation. Oxygen is normally present to some extent in columbium and can also be added or removed easily. Nitrogen is also normally present in small amounts and can also be controlled within limits.

Since it is not possible yet to remove all the nitrogen from columbium and since it is possible to remove essentially all the oxygen and carbon, initial measurements were made on the alloy system nitrogen in columbium. In this sense then, the alloys are true binary alloys. Little is known about the effects of nitrogen on the physical and metallurgical properties of columbium, so it was necessary to perform some rather elementary measurements on the specimens. These measurements are described briefly in the next section and are discussed in detail in later sections.

Scope of the Work

That internal friction is associated with diffusion of nitrogen in columbium has been known for some time. It is similar in nature to that for carbon and nitrogen in α-iron. In these latter cases, the information obtained from internal friction has been useful metallurgically,[1] and it is not too much to expect useful information from similar studies on columbium containing nitrogen. The technique of internal friction measurements is adequately described by Ké.[2]

At a frequency of 1 cps the internal friction peak for nitrogen in columbium occurs at 300°C and that for oxygen at 160°C.[3] So that all the measurements will be meaningful metallurgically, the internal friction has been calibrated by making a measurement of the damping at the two peaks and a measurement of oxygen and nitrogen content by chemical analysis. A comparison of the two gives the following calibration factor: To go from damping capacity expressed in terms of $1/Q$ to weight percent of oxygen and nitrogen in solid solution in columbium, multiply the peak values of internal friction by about 4 and 3 respectively.* Data from which these factors were calculated are presented in Table I.

The increase of electrical resistance of columbium caused by the addition of oxygen and nitrogen as interstitial impurities has been quantitatively determined. At room temperature the percentage increase is small for small additions of impurities (<0.1 wt pct); as the temperature is lowered it becomes an increasingly larger factor of the total resistance. An empirical relation has been established to express the resistivity at -195°C in terms of weight percent of oxygen and nitrogen in solid solution.

It is easy to make supersaturated solid solutions of nitrogen in columbium and to observe aging phenomena. The optimum aging temperature, as in the case for carbon and nitrogen in α-iron, occurs at the temperature for which the time necessary for a single place-change in diffusion is about 1 to 10 millisec. This means for nitrogen in columbium that significant property changes should take place for this alloy at about 400° to 500°C in reasonable time intervals. Results of such aging experiments are

* The gas analyses were made for us by the National Research Corp.

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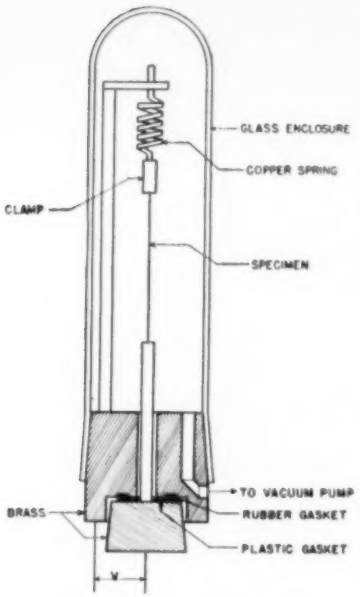

Fig. 1—Heat treatment apparatus.

presented. They show that: 1—The internal friction decreases with the time of aging. 2—The level to which the internal friction falls upon prolonged aging is a function of the temperature of aging. Utilization of this fact made it possible to calculate solid solubility as a function of temperature. 3—The electrical resistance at −195°C decreases during aging. 4—The hardness decreases during aging. This was at first somewhat unexpected, but has been verified by measurements on about eight samples aged at various temperatures.

Method of Purifying and Nitriding Columbium

For meaningful measurements to be made, it was necessary to have as nearly ideal binary alloys as possible. This meant that the interstitial impurities carbon and oxygen had to be eliminated. Furthermore, it was necessary to know that whatever nitrogen was introduced went into solid solution. A method of heat treatment was devised to do these things simultaneously. The method is a three-step process: 1—The sample is purified by heating it at 2000°C in a vacuum of about 10^{-6} mm Hg. 2—Next it is nitrided at about 1500°C. 3—Finally the specimen is reheated to 2000°C or above in the high vacuum again for several minutes, then cooled rapidly.

Table I. Data Used to Obtain Multiplying Factors to Go from Peak Value of Internal Friction to Wt Pct N_2 and O_2 in Solid Solution

Specimen	N_2, Wt Pct	O_2, Wt Pct	Q^{-1} Peak	Multiplying Factor
1	0.051	—	0.0180	2.8
2	0.063	—	0.0211	3.0
3	0.021	—	0.0068	3.1
4	—	0.037	0.0095	3.9
5	—	0.032	0.0072	4.4
6	—	0.030	0.0076	4.0
7	—	0.059	0.0143	4.1

Because of the high temperatures involved, a furnace was constructed in which the specimen itself serves as a heating element. This apparatus is illustrated in Fig. 1. A pyrex glass envelope encloses a wire specimen and heavy current leads. A current of some 25 to 75 amp is passed through the wire. Expansion is allowed by use of a copper spring under light tension. An associated vacuum system and gas storage and transfer system completes the apparatus.

The first operation is that of freeing the original material from its initial charge of nitrogen, oxygen, and carbon (these impurities are present in a typical specimen to about 0.05 wt pct N_2, 0.1 wt pct O_2, and a smaller but unknown amount of carbon†).

† The carbon peak in columbium has so far been rather elusive. It is believed that it exists at about 140°C at 1 cps. Thus it can easily be masked by the oxygen peak at 160°C when both carbon and oxygen are present together. The difficulty of preparing a sample containing a small amount of carbon and no oxygen has prevented quantitative measurement of the carbon content.

This was done by heating a 30 mil wire specimen in vacuum at 2000°C or above for some 5 min. This operation cleans the surface of the wire, straightens it, and reduces the impurity content to less than 0.002 pct C, 0.002 pct O_2, and 0.007 pct N_2. (With the exception of Table I, all values of carbon, oxygen, and nitrogen content quoted in this paper were measured or estimated from internal friction measurements.)

At this time the specimen is nitrided in half an atmosphere of either NH_3 or N_2 at about 1500°C. The time necessary for this operation is from 5 to 30 min, depending somewhat on the amount of nitrogen desired in the sample. No attempt was made to observe any difference in the rate of nitriding with the two gases; nor was an attempt made to observe the rate of nitriding as a function of temperature or gas pressure. Because of the ease with which absorbed oxygen can be removed from columbium, no serious attention was paid at this time to keep the oxygen at a very low level. The oxygen was removed and any nitrogen which may have precipitated at 1500°C put into solid solution by heating the specimen to 2000°C or higher in a vacuum of 10^{-5} mm Hg for a few minutes.

The temperatures cited above were all measured with an optical pyrometer and were corrected for the emissivity of columbium. Since deviations of 100° or more from the ones finally used make little difference in the final product, systematic errors in temperature measurement are of no significance. Furthermore, because of conduction of heat from the wire to the grips, it was clear that the specimens were not heated uniformly. Since the largest part of the heat loss is by radiation, however, the central section of the wire was essentially uniform in temperature to within approximately 100°. The ex-

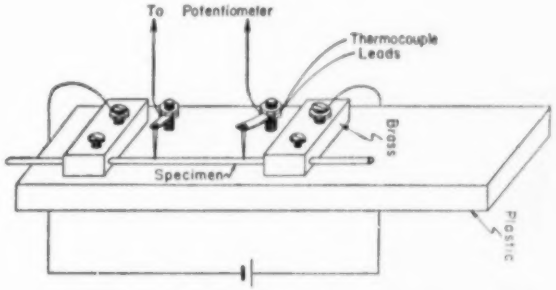

Fig. 2—Specimen holder for electrical resistance measurement.

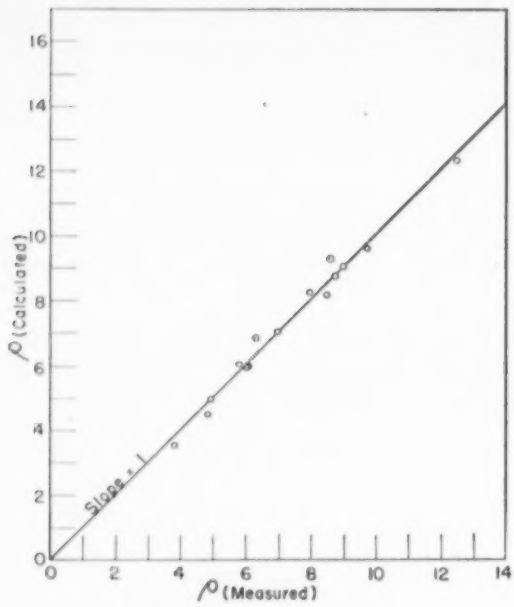

Fig. 3—ρ calculated vs ρ measured.

treme ends of the specimen, which were clearly much colder than the middle, were cut off before further measurements were made.

Electrical Resistance

The electrical resistance of a metal (except possibly in very special cases) increases upon the addition of impurities. This contribution to the resistance is virtually temperature independent. Accurate measurement of the impurity contribution at room temperature is difficult because superimposed upon it is the resistance due to thermal motion. For relatively small impurity additions, indeed, the thermal contribution may almost hide that caused by impurities. By making measurements at low temperature, however, the total resistance can be reduced while the impurity contribution is kept constant. For example, at room temperature, adding 0.05 pct N_2 in columbium causes a change in resistance of about 15 pct, whereas at −195°C, it causes a change in resistance of nearly 100 pct.

The effect on electrical resistivity of varying amounts of oxygen and nitrogen in solid solution has been measured quantitatively. Measurement by adding each of these elements in the absence of the other was attempted, but it was not possible to completely eliminate either. The total resistance of the specimen when both were present was then presumed to obey the linear equation

$$\rho_{total} = \rho_{Cb} + A \times (\text{wt pct } N_2) + B \times (\text{wt pct } O_2)$$

To find the constants A, B, and ρ_{Cb} it was necessary only to prepare three samples of varying oxygen and nitrogen content, measure their resistivities, and solve the three equations simultaneously for these constants. Additional samples served to check these calculations. The amount of nitrogen and oxygen present in each case was determined by internal friction measurements.

The resistance of a sample was measured by determining the potential drop across a sample when a known current is passed through it. The apparatus in which the specimen was mounted is shown in Fig. 2; it is immersed directly into liquid nitrogen for the measurement. Heavy current leads supply about 1 amp of current to the specimen; spring loaded potential leads are connected to a type K potentiometer. A second potentiometer measures the electromotive force across a standard resistor. From these two measurements of emf, together with knowledge of the resistance of the standard resistor, the resistance of the sample is readily calculated. Measurement of the wire cross section and specimen length complete the data necessary to calculate the resistivity.

The values of ρ_{Cb}, A, and B calculated from measurements on three selected samples give for ρ_{total} (in microhm cm) the equation

$$\rho_{t\ (-195^\circ C)} = 3 + 55 \times (\text{wt pct } N_2) + 47 \times (\text{wt pct } O_2) \quad [1]$$

A plot of ρ calculated using Eq. 1 against that value of ρ measured for all the samples is presented in Fig. 3.

At this time, these values of A and B cannot be interpreted in terms of the nature of the nitrogen or oxygen ion in columbium. When similar data are obtained for the effect of nitrogen and oxygen in other metals, it may then be possible to infer significant facts about these ions.

Aging Experiments and Solid Solubility

Many physical changes have been observed to take place in alloys upon aging, and the alloy nitro-

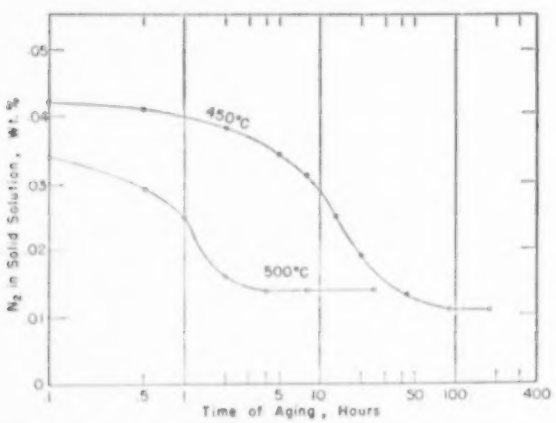

Fig. 4—Aging curves for nitrogen in solid solution in columbium.

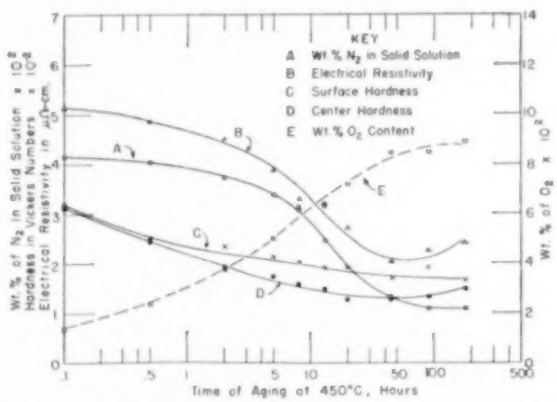

Fig. 5—Affect of aging in columbium containing nitrogen and oxygen.

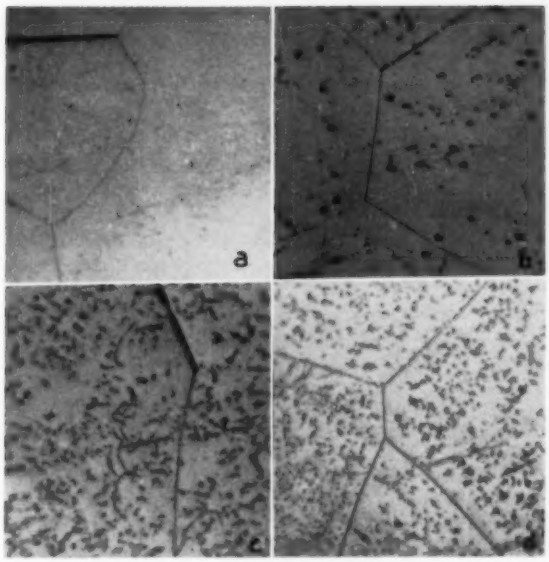

Fig. 6—Precipitation of nitrogen from solid solution in columbium during aging at 450°C. Swabbed 20 sec with 90 pct HNO_3 (70 pct) + 10 pct HF (50 pct) at 80°C. X250.

a—As quenched. c—Aged 44 hr.
b—Aged 5 hr. d—Aged 178 hr.

gen in columbium is no exception. A number of specimens of columbium were prepared containing about 0.04 pct N_2 in solid solution and aging experiments were carried out with them in the temperature range 300° to 500°C. Aging was carried out in a vacuum of about 10^{-4} mm Hg. Measurements were made of decrease in internal friction, decrease in electrical resistance, and change in hardness upon aging.

Serious attempts were made to keep the oxygen content low during the entire process. These efforts were not wholly successful. It was possible to produce specimens having fairly low oxygen content originally (<0.02 wt pct). During aging at elevated temperatures, however, it was not possible to prevent further oxygen pickup. The oxygen content of the specimens was estimated to have increased a few hundredths weight percent upon prolonged aging. The increased damping due to this oxygen in solid solution can be measured easily, but it is not easy to accurately express this increased damping in terms of weight percent oxygen. Fundamentally, this comes about because such absorbed oxygen will not be distributed uniformly radially. The calibration factor ($4 \times 1/Q$ = wt pct O_2) is not directly applicable since it is based upon a uniform solid solution of oxygen in columbium. If this calibration factor of 4 is used for this nonuniform distribution of oxygen (as is done in the plot of Fig. 5), such calculation probably overestimates the average oxygen content by a factor of 2 or more.

The amount of nitrogen in solid solution at any time was determined by the height of the relaxation peak at that time. Since the internal friction was calibrated directly in terms of nitrogen content, the amount of nitrogen in solid solution can be plotted as a function of time of aging. This is shown for two aging temperatures in Fig. 4.

A certain amount of nitrogen in solid solution does not have the same effect on electrical resistance as does that amount of nitrogen in the form of a nitride. Hence, a change in electrical resistance during aging might be expected. A change is observed and it is presented in Fig. 5. In this figure, curve *A* shows the nitrogen in solution as a function of time. Curve *E* is the approximate oxygen content vs time. *B* shows the change in electrical resistivity upon aging. These values are corrected point by point for the contribution to resistance due to oxygen content using curve *E* and the value 47 in Eq. 1. Because the oxygen content was measured only approximately, the corrections are not highly accurate. It should be emphasized, however, that even without any correction, the measured resistivity decreases steadily during aging and rises only at the end when the nitrogen has essentially reached an equilibrium division between solid solution and precipitate.

At intervals during aging small sections of the specimens were cut off. Hardness measurements were made on these sections. Surface hardness readings in Vickers numbers were taken on these sections mounted in bakelite before they were polished. After the samples were polished and etched the center hardness readings were made. These two sets of data plotted against aging time in Fig. 5 show that aging in this alloy is a softening process. It is worth noting that the surface and center hardness values are the same for the as-quenched samples and for the samples taken early in the aging process. This indicates that the method of heat treatment did result in an even distribution of nitrogen and oxygen radially in the sample. That curves *C* and *D* branch apart during aging is presumably caused by oxygen pickup at the surface of the specimen during aging. Diffusion of this new oxygen into the center is slow at this temperature, hence an oxygen-enriched case exists initially. This case extends gradually into the center of the sample so that near the end curves *C* and *D* approach each other. Although oxygen appears not to have too great an effect on the hardness‡ of columbium, brittleness was evident in wire specimens which had been purposely highly oxidized.

‡ Several specimens, containing less than 0.01 pct N_2 and from 0.01 to 0.10 pct O_2, show an increase in hardness from 86 to 122 VHN.

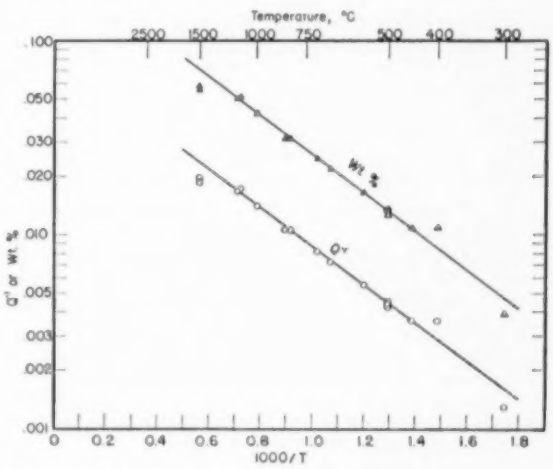

Fig. 7—Solid solubility of nitrogen in columbium as a function of temperature.

Metallographic examination of the specimen at various stages of aging at 450°C showed that the amount of precipitate increased as aging progressed. This finding substantiates the result of internal friction measurements, which show that the amount of nitrogen in solid solution decreased with time of aging. Fig. 6a shows the as-quenched specimen with practically no evidence of precipitation, whereas b, c, and d represent respectively the microstructures at the end of 5, 44, and 178 hr of aging and reveal the increasing amount of precipitate.

The final level of internal friction during prolonged aging is markedly dependent on the temperature of aging. This gives a method of finding the solid solubility in equilibrium with the nitride as a function of temperature. Fig. 7 shows the equilibrium value of internal friction at 300°C as a function of temperature of aging and the curve calculated from these data using the multiplying factor of 3 quoted above. The heat of solution calculated from this curve is 4600 cal per mol. The equation for this curve over the temperature range 300° to 1200°C is

$$C = 1.7e^{-4600/RT} \qquad [2]$$

where C is expressed in atomic pct N_2. The factor 1.7 is only as accurate as the multiplying factor taken from Table I.

References

[1] C. Wert: Phenomena Accompanying Precipitation from Solid Solutions of C and N in Alpha-Iron. *Thermodynamics in Physical Metallurgy* (1950) pp. 178-200. Cleveland. ASM.

[2] T. S. Kê: Experimental Evidence of the Viscous Behavior of Grain Boundaries in Metals. *Physical Review* (1947) **71**, p. 533.

[3] C. Ang: Diffusion of O_2 and N_2 in Nb and Ta. *Acta Metallurgica* (1953) **1**, p. 123.

Technical Note

Plastic Bending of Zinc Crystals

by G. P. Conard II, B. L. Averbach, and Morris Cohen

IT has been frequently observed that, when metal crystals are bent and annealed or when they are bent at elevated temperatures, the asterism of the Laue spots is split discontinuously into tiny intensity maxima. This finding indicates that segmented crystallites or subgrains are produced, which are relatively undistorted within themselves but which differ slightly in orientation from their neighbors.

The following viewpoints have been put forward concerning the nature of this segmentation process: 1—Crussard[1] has described the phenomenon as "recrystallization in situ." According to this mechanism, the deformed lattice recrystallizes on heating into an aggregate of comparatively strain-free subgrains separated from one another by low-angle boundaries and having nearly the same orientation as the original crystal. This process differs from the classical type of recrystallization in that the latter involves the formation of grains having quite different orientations from that of the mother crystal. 2—A similar but more detailed picture has been advanced by Cahn[2] who adopted the term "polygonization." In this interpretation, the plastic bending of lattice planes results in an excess of dislocations of one sign, but at suitable temperatures these dislocations migrate along slip planes and collect in localized regions to form an array of low-angle boundaries. Concurrently, the lattice segments between the boundaries lose their curvature and elastic strain. 3—The "cell formation" concept of Wood and coworkers,[3] unlike the two hypotheses cited, postulates that the segmentation of the lattice is basically a mode of deformation and is not an annealing phenomenon. Cell formation appears to compete more effectively with respect to the normal slip process as the deformation temperature is increased and as the strain rate is decreased.

The present work was performed on 3.2 mm diameter 99.99+ pct Zn single crystals, grown from the melt in a gradient furnace. The major impurity was 0.003 pct Fe. The crystal orientations ranged from those with basal plane parallel to the rod axis to those with the basal plane almost perpendicular to the rod axis. The specimens were bent on templates to effective radii varying from 14.2 to 1.3 cm at the temperatures from −196° to 100°C. In each case, the axis of bending was parallel to the basal plane. Subsequent annealing was carried out at temperatures from −196° to 400°C.

Back-reflection Laue pictures were taken on the convex surface of the bent specimens, before and after annealing. This procedure was found to yield better resolution of the detail in the diffraction spots than did the previously used Laue transmission technique. Some X-ray pictures of rods bent at −196° and −78°C were taken at these respective temperatures without intermediate warming to room temperature. In addition, bent crystals were acid cut[4] parallel to the basal plane, and double-crystal spectrometer rocking-curves were obtained from the etched (0001) face before and after increment an-

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This paper is based on a thesis by G. P. Conard II submitted in partial fulfillment of the requirements for the degree of Doctor of Science to the Massachusetts Institute of Technology, June 1952.

neals up to 60 hr at 400°C, with the (0001) face of an undeformed zinc crystal serving as the analyzing crystal. Laue back-reflection pictures were also taken under these conditions.

The experiments clearly demonstrated that the bending deformation produced discontinuous asterism streaks in the Laue back-reflection pictures, thus denoting a segmentation of the lattice into units of slightly differing orientation. This phenomenon was observed most commonly in specimens bent to effective radii between 8.5 and 2.4 cm. For larger radii, the bending deformation was evidently too small to yield much segmentation, whereas for radii less than 2.4 cm the severe deformation probably resulted in segmentation on too fine a scale to be resolved by the Laue technique employed here.

The occurrence of segmentation due to bending was rather insensitive to the temperature of deformation within the range investigated. It could be detected in specimens bent and X-rayed at −196°C in addition to those bent at −78° and at 100°C. These findings suggest that the crystal segments form as a part of the deformation process and do not require thermal activation for their origin, although (as will be pointed out) annealing may make it easier to detect the fine structure in the Laue spots.

In cases where the crystal orientation was such that the bending could readily cause slip in the standard $[2\bar{1}\bar{1}0]$ direction on the (0001) plane, the intensity maxima in the asterism streaks showed that boundaries of the segmented units corresponded to $(2\bar{1}\bar{1}0)$ planes; that is, the boundaries lay perpendicular to the slip plane and slip direction. The angular difference between adjacent segments varied widely, but was roughly of the order of 10 to 30 min about the $[01\bar{1}0]$ direction lying closest to the bending axis. When the conditions of deformation became complicated so that identification of the active slip system was no longer possible (for example, if the specimen inadvertently spiralled during the bending), the segmentation behavior became complex and seemed to vary in an unpredictable manner. Evidence of cross segmentation was found.

The rocking-curve for an annealed, undeformed zinc crystal showed a sharp (0001) reflection of about 6 min in half-width; but after the specimen was bent to a 1.3 cm radius at room temperature, this reflection broadened into a multi-peaked curve of about 2° in overall half-width. The numerous intensity maxima disclosed the existence of segmentation even though it was not resolved by the Laue method in this case. After the bent crystal was annealed for 5 hr at 400°C, the peaks sharpened because of a reduction in background intensity, and the Laue streaks then revealed corresponding discontinuities in the asterism.

For a specimen bent to a 6.3 cm radius, the multiple peaks of the (0001) reflection in the rocking-curve occurred at angular intervals of about 10 min. During the first few hours of annealing at 400°C, these peaks became more clearly defined; they did not disappear or change in angular position. After annealing for more than 5 hr at 400°C, there was evidence that some minor peaks disappeared while others became sharper and more intense. However, even after 60 hr at 400°C, the structure remained highly segmented, while the sharpness of the individual peaks comprising the (0001) reflection and the intensity of the intervening background approached those of the original undeformed crystal.

More complete studies with the Laue method showed that the sharpening of existing maxima in the asterism streaks on annealing increased with the annealing temperature and with the severity of the prior bending deformation. The bent crystals displayed little tendency to recrystallize in the conventional sense, except after rather complex bending followed by annealing at high temperatures.

The foregoing experiments demonstrate that zinc crystals do not undergo uniform bending, but deform in an heterogeneous manner on a fine scale to produce slightly disoriented lattice segments or subgrains, separated by boundaries in which most of the bending is concentrated. Such localized "buckling" has already been postulated by Jillson[5] and by Hess and Barrett,[6] and may turn out to be a basic mode of deformation. It provides the crystal lattice with a high degree of "plastic flexibility," and may be operative in a major way along the grain boundaries of polycrystalline aggregates where the deformation is quite complex. In any event, it must be emphasized that the segmentation occurs primarily during the deformation process. Possibly the moving dislocations of like sign tend to pile up at imperfections already present in the original crystal, thus tending to localize the bending deformation.

According to this picture, the subgrains themselves may be somewhat curved as a result of the deformation, but this lattice strain is minor compared to the concentrated bending at the subboundaries. During annealing, the lattice strain disappears as shown by the improved resolution of the maxima in the Laue spots due to the decrease in the background intensity between the maxima. It is visualized that this recovery process is achieved by the further concentration of dislocations at the subboundaries, in the manner suggested by Cahn,[2] although the main part of the "polygonization" (at least in zinc) now appears to take place during deformation prior to annealing.

With additional annealing, the subboundaries are capable of migration, thereby permitting subgrain growth to take place. These boundaries are particularly mobile under applied stress,[7-9] and could readily lead to the cell formation observed by Wood[3] and by Servi[10, 11] under creep conditions.

Acknowledgments

The zinc used for the single crystals in this work was supplied by the Platt Brothers and Co. of Waterbury, Conn. D. C. Jillson, then of the New Jersey Zinc Co., furnished some of the zinc crystals that were used in the early stages of the program. This research is part of a program sponsored by the United States Atomic Energy Commission under Contract No. AT(30-1)-1002, Scope III.

References

[1] C. Crussard: Etude de Recuit de l'Aluminium. *Revue de Metallurgie* (1944) **41**, p. 111.

[2] R. W. Cahn: Internal Strains and Recrystallization. *Progress in Metal Physics* (1950) Vol. 2, Chapter 5, p. 151. London. Butterworths Scientific Publications.

[3] W. A. Wood, G. R. Wilms, and W. A. Rachinger: Three Basic Stages in the Mechanism of Deformation of Metals at Different Temperatures and Strain Rates. *Journal* Inst. Metals (1951) **79**, p. 159.

[4] R. Maddin and W. R. Asher: Apparatus for Cutting Metals Strain-Free. *Review of Scientific Instruments* (1950) **21**, p. 881.

[5] D. C. Jillson: An Experimental Survey of Deformation and Annealing Processes in Zinc. *Trans.* AIME (1950) **188**, p. 1009; JOURNAL OF METALS (August 1950).

[8] J. B. Hess and C. S. Barrett: Structure and Nature of Kink Bands in Zinc. *Trans.* AIME (1949) **185**, p. 599; JOURNAL OF METALS (September 1949).

[9] W. A. Wood and R. F. Scrutton: Mechanism of Primary Creep in Metals. *Journal* Inst. Metals (1950) **77**, p. 423.

[10] J. Hino, P. G. Shewmon, and P. A. Beck: Effect of Simultaneous Strain on Subgrain Growth. *Trans.* AIME (1952) **194**, p. 873; JOURNAL OF METALS (August 1952).

[11] J. Washburn and E. R. Parker: Kinking in Zinc Single-Crystal Tension Specimens. *Trans.* AIME (1952) **194**, p. 1076; JOURNAL OF METALS (October 1952).

[12] I. S. Servi and N. J. Grant: Structure Observations of Aluminum Deformed in Creep at Elevated Temperatures. *Trans.* AIME (1951) **191**, p. 917; JOURNAL OF METALS (October 1951).

[13] I. S. Servi, J. T. Norton, and N. J. Grant: Some Observations of Subgrain Formation During Creep in High Purity Aluminum. *Trans.* AIME (1952) **197**, p. 965; JOURNAL OF METALS (September 1952).

Technical Note

Modifications of the Schulz Technique for The X-Ray Determination of Preferred Orientation in Rolled Metal

by M. L. Fuller and George Vaux

AN apparatus and procedure for the determination by X-ray reflection of preferred orientation of crystals in rolled metal with the Geiger counter X-ray spectrometer was described by Schulz.[1] This is an excellent procedure and we have used it continually for several years. In our use of the procedure, two modifications have been made and used during most of this period. One of these provides for automatic scanning and recording of the reflections, and the other makes possible the application of the procedure to coarse-grained specimens and permits measurement of almost all orientations without resort to the transmission technique.

[1] L. G. Schulz: *Journal of Applied Physics* (1949) **20**, pp. 1030-1033.

The automatic scanning and recording are accomplished by a motor drive of the inner ring of the Schulz apparatus (see R_2 in Fig. 2 of his paper and R_2 in Fig. 1 of this note) in synchronism with the chart recorder of the North American Philips 90° X-ray spectrometer. A rate of 10° per min is used. A scan of 180° is obtained corresponding to poles on the stereographic projection whose locus is a great circle.

The modification for coarse-grained material is accomplished by allowing a larger area of the specimen to contribute to the X-ray diffraction. In the Schulz apparatus the incident X-ray beam is confined by a slit system to rays in the plane of the spectrometer. Schulz demonstrated that this restriction of the X-ray beam permits a survey of the X-ray reflections without correction up to about 80° on either side of that specimen position in which the specimen is perpendicular to the plane of the spectrometer. This is the angle ϕ of rotation of the inner ring R_2. One of these slits is horizontal and extends across the X-ray source side of the specimen. In the modification this slit is removed, thus permitting greater divergence in the X-ray beam and the irradiation of a larger area of the specimen surface. Fig. 1 shows the apparatus with the motor drive and with the slit removed. Discontinuities in the recorded X-ray intensity plot due to the few participating crystals in coarse-grained metal are much lessened. The increased divergence does not cause reflections from other crystal planes to enter the Geiger counter slit.

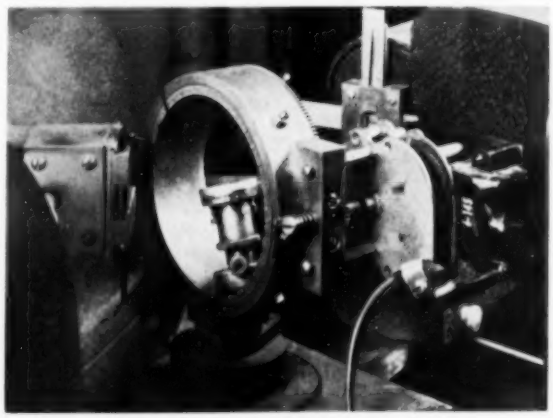

Fig. 1—Preferred orientation apparatus.

An important advantage of the original Schulz scheme is thus lost and a system for correction is required. To do this, a compact of atomized copper powder was prepared and tested by the original Schulz method for the absence of preferred orientation. The horizontal slit was then removed and a curve recorded showing the variation of intensity with angle ϕ. In our arrangement the intensity was uniform within the range ϕ equals ±30°. Beyond this the intensity fell off rapidly reaching zero at ±90°. The curve thus produced is then used to correct measurements made on preferred orientation specimens. In practice this is accomplished by constructing from this calibration curve a family of curves which, as a transparency, can be superimposed on the recorder chart to read corrected intensity directly. Not only does this method permit the handling of coarse-grained material but it also makes possible the plotting of intensities almost to the circumference of the stereographic pole figure projection. Thus, nearly the entire pole figure can be plotted without the necessity of using the transmission technique. Moreover, intensities are much greater, an advantage when surveying crystal planes of poor reflecting power.

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TN 170E. Manuscript, April 24, 1953.

AIME OFFICERS:
President—Andrew Fletcher
Vice-Presidents—T. B. Counselman, L. E. Elkins, O. B. J. Fraser, J. L. Gillson, A. B. Kinzel, J. B. Morrow
President-Elect—L. F. Reinartz
Treasurer and Controller—G. I. Brigden
AIME STAFF:
Secretary—E. H. Robie
Ass't. Secretaries—J. B. Alford, H. N. Appleton, E. J. Kennedy, Jr., Ernest Kirkendall, R. E. O'Brien
Ass't. Treasurer—P. J. Apol

aime NEWS

H. N. Eavenson Wills $150,000 to Institute

Terms of the will of the late Howard N. Eavenson, President of the Institute in 1934, were recently made known to AIME Directors. The money will be available as a trust fund after the death of Mrs. Eavenson, and the income is to be used for the following purposes: (1) To defray the cost of publishing papers of interest to members of the Coal Div. (2) To establish the Howard N. Eavenson Award to amount to at least $500, with an engrossed certificate, to be given from time to time to a person who has contributed the most to the advancement of the coal industry. (3) For other purposes of the Coal Div. if the annual income is not used as specified in (1) or (2).

This large gift will bring the total general endowed funds of the AIME to approximately $960,000. The principal other Funds are the James Douglas Library Fund, $110,000; Rocky Mountain Club Fund, $114,000; Seeley W. Mudd Fund, $106,000; George D. Barron Fund, $133,000; and Henry L. Doherty Fund, $98,000.

MGGD Honors Approved By Board

At its meeting on June 17, the Board of Directors gave tacit approval to a proposal that a Lectureship and an Award to young men for the best paper in the field of the Mining, Geology, and Geophysics Div. be established. C. M. Cooley, Secretary of the Mining Branch, was directed to develop the details of the plan. The proposal emanated from the MGG Div. The Lectureship will probably be named in honor of D. C. Jackling and will be an annual invitational address by an outstanding man in the field of the Div., to be a feature of the Annual Meeting. Similar Lectureships have long been established by the Institute of Metals and the Iron and Steel Divs.

The other award will be granted to the person or persons, not over 40 years old, who has or have submitted an outstanding paper in the field of the MGG Div. A cash prize accompanied by a certificate is planned, the award to be made at the annual Mining Branch Dinner. Complete details remain to be worked out and approved.

AIME Nominating Practice To Be Reviewed

Following suggestions made by the Chicago Section, AIME, and the Minerals Beneficiation and Coal Divs., that a committee be appointed to review the present method of nominating AIME officers, the Board, at its June 17 meeting, named the following to serve on such a committee: J. B. Morrow, Chairman; Clayton G. Ball, L. E. Elkins, W. M. Peirce, W. B. Stephenson, and Andrew Fletcher, ex officio. The present procedure is detailed in Article IX of the Bylaws (page xlv of the current Directory) and in "Information and Advice to Members of the AIME Nominating Committee" (page xxxi). The committee will appreciate hearing from individual members or groups who have constructive suggestions to offer for improvement, or who wish to commend the present rules. These were extensively revised just three years ago by the Board, following recommendations of another committee appointed for the purpose.

Petroleum Scholarship Renewed for 1953-54

Jack I. Laudermilk advises that the Socony-Vacuum Oil Co. will again support financially the scholarship offered to senior petroleum engineering students for the first time last year. The colleges with petroleum engineering curricula have been notified. High scholastic achievement and intention to enter the petroleum industry immediately on graduation are the principal qualifications for the $750 award. Administration of the scholarship is in the hands of a committee consisting of Allison Butts, Chairman, Paul R. Turnbull and D. V. Carter.

Hotels Scheduled For Annual Meeting

Present plans are to hold the Metals Branch technical sessions, with the exception of the Howe and IMD Lectures, in the McAlpin Hotel in New York, Feb. 15 to 18, 1954. The Metals Branch luncheons and dinners will also be held in that hotel. It is believed that all other events can be accommodated in the Statler Hotel, except the Annual Banquet, which will be in the Waldorf-Astoria on Feb. 17. The McAlpin is just a block east of the Statler and can be reached by a subsurface passage.

With the planned enlargement of the Roosevelt Hotel in New Orleans, it is expected that the Annual Meeting can be accommodated in that city in February 1957. Should that not prove feasible, the meeting will be held in Dallas, where a new Statler Hotel should be ready by that time, assuring sufficient accommodations.

The 1955 meeting will be held in the Conrad Hilton Hotel, Chicago, and the 1956 meeting in New York.

RESEARCH IN PROGRESS

Research personnel are reminded of the Institute of Metals Div. Research in Progress session planned for the Fall Meeting in Cleveland. Abstracts of proposed papers not exceeding 200 words in length are to be submitted to Institute headquarters prior to Aug. 1, 1953, for inclusion in the September issue of JOURNAL OF METALS. Abstracts not received in time for publication in the September issue may, nevertheless, be presented if received prior to Sept. 15, 1953, according to B. L. Averbach, IMD Program Committee.
The Program Committee urges those interested to avail themselves of the opportunity of participation in this program in order that new research information be presented for discussion.

Board to Take Action On Proposed Bylaw Changes

Local Sections

At the meeting of the Inter-Branch Council in Los Angeles, Feb. 15, 1953, a resolution was passed recommending that the AIME Board of Directors change the bylaws so that more than one Local Section in a given geographical area be permitted. The reasoning was that in certain Local Section areas, Divisional or Branch interests could be served better if a Local Section devoted to their specific interests was organized. Heretofore, Local Sections whose membership had diverse professional interests either had little to offer members in their particular professional field, or operated through loose sponsorship of small groups or subsections. In some Sections such organization was satisfactory, in some others not.

The Executive and Finance Committees considered the resolution at their meeting on April 15, and the Board discussed the matter further at the meeting of June 17. No particular objection was offered to the idea of overlaying Local Sections provided the Council of Section Delegates is not unduly enlarged thereby and that the cost of supporting Local Section activities does not increase. In any case, the proposed change in the bylaws would be permissive only, as to establishing overlaying Local Sections, and no Section could be established or continue in existence without approval of the Board. This would give the Board authority to take action on canceling a Local Section if cause therefor developed. It was generally agreed that Section Delegates should represent areas rather than Local Sections if the plan were in effect.

The Board voted to propose to delete the following words from Article XI, Section 3, of the bylaws (page xlvii, 1st column, of the 1952-53 Directory): "Only one Section shall be authorized in any one locality or district and".

The Board will vote on this change in the bylaws at its meeting in Seattle on Sept. 22. If the change is authorized at that time, members will be advised of the procedure to be followed in setting up new Local Sections in areas already covered.

Meeting Papers

Heretofore, the AIME bylaws have not been specific as to the ownership of papers presented at Institute meetings. The only such reference in the bylaws is in Section 3 of Article XI, which states that "Papers presented at Local Sections, and discussions thereon, if reported, shall be the property of the Institute. Such papers shall not be published elsewhere in extenso without permission of the Board." Questions have often arisen as to publication rights of other papers.

Three years ago a committee consisting of H. A. Meyerhoff, Chairman, with R. M. Foose and C. C. Long, was named to study the matter of the ownership and release of technical papers presented at AIME meetings. Reports of the committee, and staff discussions thereon, have been recorded in the minutes of various meetings of the Board. Proposed amendments to the AIME bylaws, which will be voted on at the Sept. 22 meeting of the Board, seem to meet with general approval, and the Board, at its meeting on June 17, directed that they be published.

It is proposed to amend Article 10 (page xlvi in the current Directory) by adding Section 2, which would read as follows:

All papers presented before meetings of the Institute — Annual, Regional, Branch, Divisional, and Local Section — are the property of the Institute, except those previously published elsewhere, those withheld from publication by the author, or those released by the Secretary of the Institute.

It is also proposed that the sentence above quoted in Article XI, Section 3, be amended as follows:

Papers presented at Local Section meetings, and discussions thereon if reported, shall be the property of the Institute, except those previously published elsewhere, those withheld from publication by the author, or those released by the Secretary of the Institute. (The sentence immediately following, beginning "Such papers," is to be deleted.)

Apportion Duties Of Institute Officers

Heretofore, AIME Vice-Presidents and the President-Elect have been given no specific duties or responsibilities, nor has the Nominating Committee had any instructions as to the selection of Vice-Presidents. The President each year has had to assume all the burden of travel to Local Sections and Student Chapters, and with well over a hundred such visits expected, Presidents have done well to reach a half of the Sections and a quarter of the Chapters.

A committee, consisting of L. E. Young, Chairman, with Leo F. Reinartz and O. B. J. Fraser, was recently appointed to suggest a better division of duties and responsibilities among the highest officers of the Institute. Their report, made at the June 17 meeting of the Board follows:

"(1) Recommend no changes in districts at this time. (2) For the present, retain six Vice-Presidents. (3) In 1953, Vice-Presidents, President-Elect, and President shall constitute a committee, which, for the present, will agree voluntarily to arrange a schedule with the Secretary of the Institute to visit the Sectional, District, and National Conferences, and as many Student and Local Chapters as possible this year. It is understood and deemed desirable that the President is privileged to call upon any Director in a given area to act as his representative in case he, the President-Elect, or one of the Vice-Presidents cannot attend certain meetings in that area. (4) Apportion the present ten Directoral Districts to the President-Elect and the six Vice-Presidents in such a way that each area served by an officer of the Institute would have equal membership. (5) Instruct future Nominating Committees to select candidates for the Vice-President's office in such a way that there will be a more equitable distribution of such individuals according to the territories of the AIME. (6) The officer chosen for a given district should interest himself in the Local and Student Chapters in his district in such a way that he may help in solving local problems, encourage new memberships, and in general assist in improving the services of the Institute to the members in his area, as well as presenting to the Board of Directors the views and aspirations of the membership he represents. (7) It is proposed that, after 1953, at the beginning of each Institute year the President shall call together the Vice-Presidents and President-Elect to discuss with them and the Secretary of the Institute basic Institute policies, practice, financial condition, membership problems, future program, and any other information of value to the officers. The Secretary shall prepare each year a manual of pertinent information about the Institute's policies and practices for use by the officers and Directors in that year. (8) It is proposed that, at the above-mentioned meeting, a schedule of visits to various local, district, and national meetings shall be presented by the Secretary for discussion, approval, and action by the group."

The report was accepted by the Board and the Secretary was directed to proceed immediately to carry out the recommendations.

Increase Local Section Appropriations

Reduced appropriations to Local Sections for 1953 were not questioned by a majority of the Sections but 15 or so expressed opposition to the action for one reason or another. The Board considered these objections at its meeting on June 17, and voted to increase the current distribution to a total approximately the same as that distributed in 1952 and the immediately preceding years, or to approximately $10,000. The earlier allotment had totaled $7700 after increases had been made in four cases. The Committee was to make a further study of the matter in July and to recommend increasing the allotments to some of the Local Sections whose treasuries appear to be most in need of support. It is expected that the Council of Section Delegates will study the matter carefully, discuss it at its meeting next February, and make a recommendation to the Board as to the degree of financial support to be accorded Local Sections in the future.

AIME Supports EJC In UPADI Financing

AIME Directors have voted the sum of $603 from the Eilers Fund as a contribution to Engineers Joint Council which will be used to finance UPADI (Union Panamericana de Asociaciones de Ingenieros) activities on a restricted scale during the current year. The contribution, totaling some $4500, is in the form of a loan to the UPADI Fund. When financing is completed it is expected that the loan will be repaid.

Societies Plan New Engineering Building

For several years there has been discussion about securing a new building to house the societies now occupying the Engineering Societies Building in New York. Space in this building is inadequate and its facilities outmoded, it being 47 years old. No definite conclusion has yet been reached about a new building but present activity indicates that a definite proposal will be offered the Founder Societies before the end of the year. Within three to five years a new building may be ready for occupancy.

Preliminary plans are for a new building with 180,000 sq ft of usable floor space, compared with 118,000 in the present building. Additional societies can then be accommodated. About $2 million is available from anticipated sale of the present building and accumulated reserves of United Engineering Trustees that could be utilized for the purpose. A new site might cost $1,500,000, possibly much less. Something on the order of $6 million for the entire new building project is envisaged.

Though the preference is for a building in mid-town New York, headquarters in other cities will also be considered. An active project for an engineering center in Pittsburgh is under way and a definite proposal is expected shortly. It is hoped that the land required for the new building may take the form of a gift, and that possibly a substantial part of the money required for the entire project may be raised by contributions. An expression of opinion as to the best location for a new building is invited from AIME members.

AIME Represented At Secretaries' Meeting

On June 5 and 6 between 30 and 40 representatives of national and local engineering societies met at the Haddon Hall Hotel in Atlantic City for the annual meeting of the Council of Engineering Society Secretaries. O. Laurence Angevine, of the Rochester Engineering Society, presided, as Council president. Papers were read on Managing Publications; Meeting Increased Costs in Society Operation; Promotional Material; Aims, Purposes, and Operation of ASTM; and Organizing for Community Activity Under ECPD Training Program. Highlight of the program was a panel of discussion of Modern Office Procedure, in which the new equipment and methods in use by the AIME attracted much attention. The AIME had three representatives present: E. H. Robie, Secretary; P. J. Apol, Business Manager; and H. N. Appleton, Assistant Secretary for Institute Activities. Officers elected for the coming year are as follows: Ernest Hartford, executive assistant secretary ASME, president. Edward H. Robie, secretary AIME, vice-president. M. C. Turpin, secretary American Society of Refrigerating Engineers, secretary. Charles S. Doerr, secretary Engineers Club of Philadelphia, treasurer. T. J. Ess, managing director, Assn. of Iron and Steel Engineers, director for three-year term. Other directors continuing to serve are: J. Earl Harrington, secretary, Western Society of Engineers; H. H. Henline, secretary, AIEE; and O. L. Angevine, secretary of the Rochester Engineering Society.

EJC To Be Enlarged

Enlargement of Engineers Joint Council to include other engineering societies makes certain changes in its constitution advisable. At the June 17 meeting of the AIME Board, these changes, giving the qualifications under which a national engineering society might become a constituent body, were approved. They would provide: (1) The corporate or voting membership shall be confined to individual members (not corporations or company members). (2) A majority of individual members shall be either graduates of engineering colleges of recognized standing or shall be licensed or registered by a State Board of Registration for Professional Engineers. (3) The society shall have a total membership of at least 5000 individual members of which the majority must meet the above requirements. (4) Request for admission shall receive the affirmative vote of not less than two thirds of the constituent societies of the Council.

At present, EJC comprises the ASCE, AIME, ASME, AIEE, AIChE, Society of Naval Architects and Marine Engineers, American Society for Engineering Education, and American Water Works Assn.

New Subsection Formed

A Subsection of the St. Louis Local Section has been authorized, to be known as the Arkansas-Bauxite Subsection. The new Subsection embraces all that part of Arkansas north of and including the following counties: Polk, Montgomery, Hot Spring, Grant, Jefferson, Arkansas, and Phillips. A part of this territory had formerly been in the field of the Lou-Ark and Tri-State Sections.

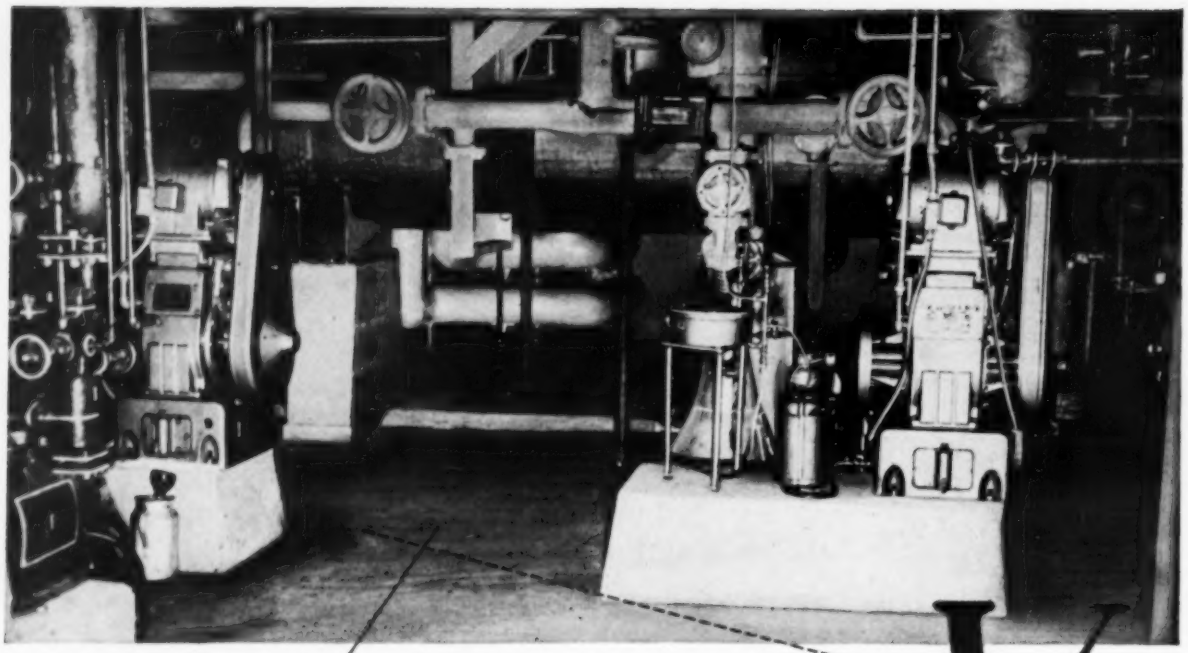
Directory Issued By Petroleum Branch

The Petroleum Branch has just issued an up-to-date directory of its members. Copies may be obtained by addressing the office of the Petroleum Branch, 800 Fidelity Union Bldg., Dallas 1, Texas.

A supplement to the all Institute Directory, giving a list of the 1953 officers of the Institute and its Branches, Divisions, Local Sections, and Student Chapters, committee personnel, and representatives, will be mailed to all paid-up AIME members on or about July 1.

ANNUAL MEETING PAPER DEADLINE

Sept. 15, 1953 is the deadline for all Institute of Metals Div. papers for the 1954 New York Annual Meeting and the deadline for all Iron and Steel Div., and Extractive Metallurgy Div. papers to be prepublished.



Stokes Microvac Pumps in machine room at Research Laboratories, Inc., St. Joseph, Mo., including diffusion type booster pump, condenser, and oil clarifier. Note relatively small size of the Stokes 8" Vacuum Valve (top-center) compared with other 6" vacuum valves at right and left.

Stokes Microvac Pumps...
basic to Vacuum Processing

High volumetric and mechanical efficiency makes these famous pumps economical and reliable units in any vacuum system.

Capacities of Stokes Microvac Pumps run from 15 to 500 cfm . . . pressures to 10 microns absolute. Power consumption is low and the top-mounted motor contributes to compact design requiring minimum floor space.

Lubrication of the four moving parts (including the exhaust valve of corrosion-resistant Teflon) is fully automatic. There are no stuffing-boxes or grease-fittings, and no packing.

Parts are precision-finished, standard and interchangeable. Freedom from wear assures years of trouble-proof service.

Stokes is the only manufacturer of equipment for complete vacuum systems, including Microvac mechanical pumps, oil diffusion pumps, McLeod Gages and Vacuum Valves.

Consult with Stokes on the application of vacuum to vacuum sintering, melting, de-gassing, heat treating, inert gas purging, vacuum metallizing, and to other purposes for which vacuum deserves exploration.

F. J. Stokes Machine Company, Philadelphia 20, Pa.

Send for new Vacuum Calculator for rapid slide-rule calculations. Includes standard ABCD log scale. Also send for Catalog 780, "Stokes Microvac Pumps for High Vacuum," with copious reference material.

STOKES

STOKES MAKES: High Vacuum Equipment, Vacuum Pumps and Gages / Industrial Tabletting, Powder Metal and Plastics Molding Presses / Pharmaceutical Equipment

Personals

S. L. HOYT

S. L. Hoyt has retired as technical advisor at Battelle Memorial Institute to engage in consulting practice. He will remain as a part time consultant for Battelle. He joined Battelle in 1939. Prior to that he had been associated with the A. O. Smith Corp. and General Electric Co.

Richard W. Lyke has been promoted to assistant plant manager of the Niagara plant, Hooker Electrochemical Co.

Howard G. Grim, works manager, Heppenstall Co., has been promoted to general manager of operations. **Paul H. Daley** is now assistant general manager.

Frank Warga has been promoted to the new post of general foundry foreman, AiResearch Mfg. Co., Los Angeles. Mr. Warga was formerly foreman of the aluminum foundry,

Marion L. Pickelsimer has been appointed to the staff of the Oak Ridge National Laboratory, Oak Ridge, Tenn.

John J. Grebe was appointed director of nuclear research and development, Dow Chemical Co., Midland, Mich.

Solomon Lieb has resigned from DMPA, program development div., to accept a position with the Corp. Minera de Bolivia as general superintendent of concentration.

Richard S. Newlin, a director and vice-president, was elected president, Inspiration Consolidated Copper Co., New York. **H. Myles Jacob,** secretary and treasurer, was elected a director.

Robert J. Johnson has resigned as plant maintenance and research metallurgist, Republic Steel Corp. He has joined the Round Chain Companies, Cleveland, as chief metallurgist.

Herman Zeigler, formerly production superintendent, has been promoted to general plant manager in charge of all operations, Wisco Aluminum Corp., Detroit.

Albert Easton White, director, Engineering Research Institute, University of Michigan, has retired after serving for 33 years. Professor White began his career at Jones & Laughlin Steel Co., Pittsburgh. In 1911 he joined the University of Michigan as an instructor.

Wilbur T. Blair was appointed vice-president and treasurer of the Sharon Steel Corp.

Max Huber has resigned from the Georges Fischer Co., Schaffhausen. He is now associated with the Battelle Memorial Institute, Geneva, Switzerland.

J. Ogden has resigned from I. Stern & Co. to accept a position with the Baker & Co., Inc., Newark, N. J.

D. I. BROWN

Darwyn I. Brown, technical editor of The Iron Age, has resigned to accept the position of market development manager, Koldflo div., Mullins Mfg. Corp., Salem, Ohio. Mr. Brown had been associated with Youngstown Sheet & Tube Co., Carnegie-Illinois Steel Co., and U. S. Steel Corp.

Harry T. Marks has been named administrative vice-president, Ferro Corp. Mr. Marks had been vice-president in charge of foreign operations.

E. E. Moore has been appointed assistant to president and vice-president, U. S. Steel Corp., Pittsburgh. Mr. Moore had been vice-president, industrial relations, administrations.

W. Tom Moore has been named as executive assistant in the atomic power div., Babcock & Wilcox Co. Mr. Moore has been associated with the firm since 1926.

Robert E. Powers is with the Freyn engineering dept., Koppers Co., Inc., Chicago.

E. Finley Carter has been appointed vice-president and technical director, Sylvania Electric Products, Inc. **Howard L. Richardson** was named vice-president in charge of engineering operations. Mr. Carter has been a vice-president since 1945 and Mr. Richardson, since 1951.

A. F. Franz, president of the Colorado Fuel & Iron Corp., recently received the honorary degree of Doctor of Commercial Science from St. Bonaventure University.

William R. Veazey has retired after 37 years service with the Dow Chemical Co., Midland, Mich.

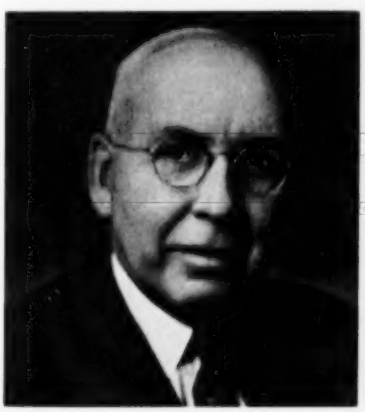
H. W. Franz is now plant manager for Colonial Aluminum Smelting Corp., Columbia, Pa.

J. H. Kelley, assistant superintendent, open hearth and bessemer dept., Bethlehem Steel Co., Sparrows Point, Md., was awarded the American Iron and Steel Institute Medal. The award is given annually for a paper of special merit in connection with the activities of the iron and steel industry.

E. C. Clark, assistant director of the research and engineering dept., Air Reduction Sales Co., has been appointed director of operations. Mr. Clark has been associated with the firm for 24 years.

E. Gardner Counselman is sales engineer with the Dravo Corp., New York.

T. S. Fuller has been appointed consultant for the research and metallurgical departments of Heppenstall Co., Pittsburgh. Mr. Fuller recently retired after 42 years of service with the General Electric Co.



T. S. FULLER

Howard P. Eells, Jr., president, Basic Refractories Inc., was awarded the honorary Doctor of Laws degree from the University of Nevada.

John M. Parks, formerly of the Armour Research Foundation of the Illinois Institute of Technology, is now associated with the Air Reduction Co., Inc., research laboratories Murray Hill, N. J., as manager of the metallurgical div.

J. R. GORDON

J. Roy Gordon has been elected vice-president and general manager of Canadian operations of the International Nickel Co., of Canada, Ltd. Mr. Gordon has been an assistant vice-president since 1947. He was appointed assistant general manager of the company's Canadian operations in 1952. He was also named a director of the company.

J. George Gange has been elected vice-president and comptroller, U. S. Smelting Refining & Mining Co., Boston.

William J. Priestley, vice-president and director, Union Carbide & Carbon Corp., was awarded the Lehigh Alumni Award, by the Alumni Assn. of Lehigh University.

Harry T. Graham, general sales manager, has been named vice-president, General Refractories Co., Philadelphia. **Richard E. Longacre** succeeds him as general sales manager.

S. J. Sindeband was elected president of the Mercast Corp., New York. Mr. Sindeband had been executive vice-president.

Albert Muller, manager of the metallurgical div., Air Reduction Co., Inc., has been appointed director of metallurgical research for the company. Dr. Muller joined the research laboratories of Air Reduction in 1946 as head of the welding section. In 1951 he was made manager of the metallurgical div.

James C. Hicks, Kaiser Aluminum & Chemical Corp., San Jose, Calif., is director of refractory research. He had been manager, technical service dept.

J. M. Van Winckle has been appointed chief engineer, Quebec Iron & Titanium Corp. He will be located at the Sorel works.

Harry C. Slagle, manager of Aluminum Co. of America's Chicago works, has been transferred to Pittsburgh as manager of Alcoa's shop training program. He will be succeeded by **R. E. Sheffer,** staff assistant to the general manager of the company's fabricating div.

J. T. MacKenzie, technical director, American Cast Iron Pipe Co., Birmingham, Ala., and **Jerome Strauss,** vice-president, Vanadium Corp. of America, New York, received 1953 Awards of Merit from the American Society for Testing Materials.

Carl J. Westling has been appointed director of engineering for Salem-Brosius, Inc., Pittsburgh.

Joe S. Turner has resigned as research metallurgist, steel and tube div., Timken Roller Bearing Co., Canton, to accept a position as materials engineer with Coleman Co., Inc., Wichita, Kan.

Harold W. Paxton has been named assistant professor of metallurgy at Carnegie Institute of Technology, Pittsburgh. He had formerly been with the dept. of metallurgy, Birmingham University, Birmingham, England.

M. D. HASSIALIS

M. D. Hassialis, professor of mineral engineering and executive officer of the School of Mines, Columbia University, received the honorary degree of Doctor of Science from Bard College.

Richard C. Diehl, president of Chase Brass & Copper Co., Inc., has been elected president of the Copper & Brass Research Assn.

Neil Franklin Meredith has joined Basic Refractories Inc., Cleveland, as technical assistant to vice-president in charge of operations and engineering. Mr. Meredith was formerly ceramic engineer for the spark plug div., General Motors Corp.

Arthur V. Peterson, formerly with the Atomic Energy Commission, has joined the staff of the vice-president in charge of engineering, American Machine & Foundry Co.

Theodore E. Olt, director, research laboratories, Armco Steel Corp., Middletown, Ohio, has been elected a member of the ASTM board of directors for a three-year term.

Henry J. Fisher, metallurgist with the physical metallurgy div., Canadian Dept. of Mines and Technical Surveys, has recently been awarded the degree of doctor of engineering by Yale University.

Clem H. Hohner has been appointed district manager of the Udylite Corp., southeast sales district.

H. L. Ingram, Jr., special representative, Washington, D. C., Air Reduction Sales Co., has been appointed manager of the technical development dept., New York. Mr. Ingram has been with Airco for 18 years.

Herbert H. Uhlig has been promoted to the rank of full professor in the dept. of metallurgy at Massachusetts Institute of Technology. **Benjamin L. Averbach** was promoted to associate professor in the same dept.

Walter R. Hibbard, Jr., has been appointed manager of the newly established alloy studies section in the General Electric research laboratory's metallurgical research dept.

Philip I. Wolf has been appointed sales engineer, research and control instruments div., North American Philips Co., Inc. Previously, he had been assistant sales manager in the New York office of Picker International Corp.

Lawton Howell was appointed to the position of works controller at the Sanderson-Halcomb works, Syracuse, N. Y., Crucible Steel Co. of America.

Harold B. Ressler, chairman of the executive committee of Joseph T. Ryerson & Son, Inc., recently retired from active service. He will remain a director of the firm. Mr. Ressler joined Ryerson in 1905.

John A. Marsh, assistant vice-president and manager of operating dept., International Nickel Co., Inc., has been elected vice-president of the company. Mr. Marsh is in general charge of all plant operations in the United States. He became associated with Inco in 1928 as a laboratory assistant at Huntington, W. Va.

S. C. Massari has resigned as technical director of the American Foundrymen's Society, Chicago, to become general manager of the foundry div., Hansell-Elcock Co. **Hans J. Heine,** formerly chief metallurgist with Rockwell Mfg. Co., has been named acting technical director.

E. S. Bunn, metallurgical manager, aluminum div., Revere Copper & Brass, Inc., has been transferred from Baltimore to the New York office.

E. J. Byrnes, Jr., has been appointed assistant general manager of sales, eastern div., Colorado Fuel & Iron Corp.

Alexander Gobus, director, nondestructive testing dept., North American Philips Co., Inc., represented the ASTM at a welding conference held in Copenhagen. He is visiting Philips laboratories in Holland and other countries on the continent.

Birger L. Johnson, Jr., is in charge of the metallurgical laboratory, Latrobe Steel Co., Latrobe, Pa. He had been chief metallurgist, research div., Mack Mfg. Corp., Plainfield, N. J.

John E. Seward has been made blast furnace practice engineer, Indiana Harbor works, Youngstown Sheet & Tube Co., E. Chicago, Ind. He had formerly been relief foreman, blast furnace dept., Wisconsin Steel Co., Chicago.

G. B. Webb was appointed senior process engineer for Walter Kidde Nuclear Laboratories, Garden City, Long Island, N. Y.

Thomas D. Cartledge has been elected vice-president of Union Carbide & Carbon Corp., New York. Mr. Cartledge has been president of Linde Air Product Co. since May 1952. He is also a director and president of Dominion Oxygen Co., Ltd.

Thomas W. Gabriel has been appointed assistant vice-president in charge of sales for Jessop Steel Co., Washington, Pa.

Edward E. Hill has been named assistant chief inspector for the Worcester Pressed Steel Co., Worcester, Mass. Mr. Hill has been associated with the firm for 10 years.

Frederick Walker, American Smelting & Refining Co., Los Angeles, has been transferred to the Federated Metals div., New York.

E. J. Perry has resigned from Falconbridge Nickel Mines Ltd., to join the staff of Giant Yellowknife Gold Mines Ltd., Northwest Territories, Canada.

George H. McCleskey has been promoted to product metallurgist, heavy forgings, metallurgical div., Homestead district works, U. S. Steel Corp., Munhall, Pa.

Obituaries

Harlan S. Emlaw (Member 1898) died on Feb. 5, 1953. He was a retired mining engineer, formerly president of American Potash & Chemical Corp. Born in Grand Haven, Mich., Mr. Emlaw received his M.E. from Michigan College of Mining and Technology in 1895. He first worked as a surveyor in Cripple Creek, Colo.; then as an engineer with Basin & Bay State Mining Co. in Montana and with the Washoe plant of Anaconda Copper Mining Co. For several years Mr. Emlaw was general superintendent of mines for Cerro de Pasco Corp. in Peru. At various times he was vice-president of the Fresnello Co. and president of Golden Queen Mining Co., Tri-State Zinc, Inc., and Buell Engineering Co. Mr. Emlaw was a Legion of Honor Member of AIME.

Ralph E. Gruber (Member 1920) died in Lisbon, Portugal after a short illness. He had been directing manager of the Portugal American Tin Co. and vice-president of the House of Portugal Inc., and the Maderia Wine Co., San Francisco. Born in Warren, Pa., he was employed by various mining companies and did examination work in Oregon. For the past 30 years he had been employed by the Portugal American Tin Co., spending most of his time in Portugal but making frequent trips to California.

Charles Lindmueller (Member 1916) died in Chicago on May 3, after a long illness. He was born in 1874 at Cleveland. He attended the Case School of Applied Science. In 1911 Mr. Lindmueller became associated with the Metal & Thermit Corp., and served as general manager for 33 years. He was a member of the American Chemical Society and a director of the Manufacturers' Assn. of East Chicago.

Francis M. Walters, Jr. (Member 1931) died on Apr. 18, 1953. A graduate of University of Missouri, he received his doctorate in physics in 1920. For a few years Dr. Walters was an instructor in physics at the University of Montana. In 1918 he was an assistant physicist at the Bureau of Standards and later became an associate physicist. For a time he was located in Shanghai as professor of physics with St. John's University. He returned to the United States as an associate physicist with the Bureau of Standards. In 1924 Dr. Walters was named director of the bureau of metallurgical research at Carnegie Institute of Technology. He remained here for several years, and then joined the Youngstown Sheet & Tube Co. At the time of his death he was located at Los Alamos, N. Mex.

NECROLOGY

Date Elected	Name	Date of Death
1936	John A. Burgess	May 22, 1953
1924	H. C. Forney	June 18, 1953
1944	O. C. Garst	May 25, 1953
1907	Frederick G. Lasier	Unknown
1905	Robert H. Stewart	December 1952
1896	W. D. Thornton	June 9, 1953
1927	John W. Wilson	Feb. 26, 1953

Proposed for Membership
— Metals Branch AIME —

Total AIME membership on May 31, 1953 was 18,822; in addition 1227 Student Associates were enrolled.

ADMISSIONS COMMITTEE

O. B. J. Fraser, Chairman; Philip D. Wilson, Vice-Chairman; F. A. Ayer, A. C. Brinker, R. H. Dickson, Max Gensamer, Ivan A. Given, Fred W. Hanson, T. D. Jones, G. W. Lutjen, E. A. Prentis, Sidney Rolle, J. T. Sherman, F. T. Sisco, R. L. Ziegfeld.

The Institute desires to extend its privileges to every person to whom it can be of service, but does not desire as members persons who are unqualified. Institute members are urged to review this list as soon as possible and immediately to inform the Secretary's office if names of people are found who are known to be unqualified for AIME membership.

In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; A, Associate Member; S, Student Associate.

California
San Mateo—Adams, Robert M. (A)
Santa Monica—Born, William F., Jr. (J) (R. C/S—S-J)
Sherman Oaks—Waisman, Joseph L. (M) (C/S—A-M)

Illinois
Chicago—Aeberly, Robert A. (M)
Chicago—Van Meter, Elgin (J) (R. C/S—S-J)

Maryland
Baltimore—Harrison, Eleanor H. (M)

Michigan
Ferndale—Reen, Orville W. (S)

New Jersey
Newark—Robert E. Bannon (M) (R. C/S—J-M)

New York
Buffalo—Northrup, Harry H. (M)
New York—Yeoman, Donald C. (J)
Tuckahoe—Dean, John G. (M)

Ohio
Hubbard—Pollock, William B., II (A)
Oak Hill—Hitchcock, Maurice R. (A)
Steubenville—MacDonald, A. John III (J) (R. C/S—S-J)
Youngstown—Fogoros, Nick (A)

Pennsylvania
Bala-Cynwyd—Roberts, John S. (M) (R. M)
Butler—Heckett, Eric H. (A)
Glenshaw—Henninger, Robert C. (A)
Harrisburg—Willis, James L. (M)
Hazleton—Specht, Jack S. (J)
Kennywood—Ross, James (A)
New Kensington—Blean, George G. (A)
Norristown—Moore, Charles D. (A)
Palmerton—Marvin, James A., Jr. (M) (C/S—A-M)
Pittsburgh—Allardice, James B. (A)
Pittsburgh—Antonelli, John J. (A)
Pittsburgh—Edgar, Clement B. (M)
Pittsburgh—Flaherty, Joseph H. (A)
Pittsburgh—Garvin, Edgar W., Jr. (A)
Pittsburgh—Glasgow, John A. (A)
Pittsburgh—Rath, Robert A. (A)
Pittsburgh—Reed, Thomas F. (A)
Pittsburgh—Richardson, Robert M. (A)
Pittsburgh—Wolcott, Roger M. (A)

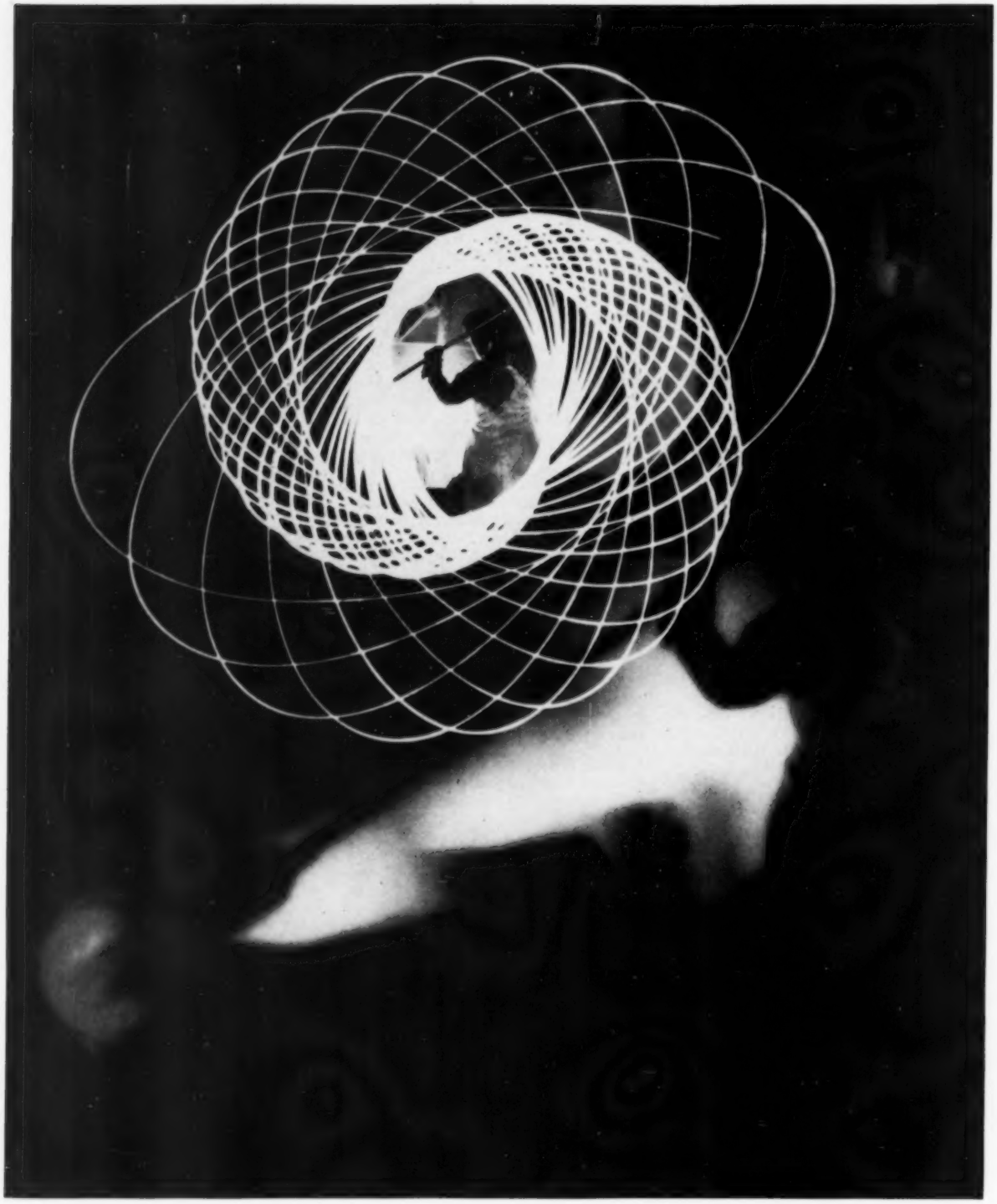
Tennessee
Chattanooga—Genung, Clayton R. (M)
Ooltewah—Miller, Ralph M. (M)

Texas
Houston—Wilson, Donald E. (M)

Canada
Hamilton—Hetrick, Robert (A)
Ontario—Joyce, Douglas (A)
Toronto—Bronskill, Beverley G. (A)

India
Jamshedpur—Bucknall, Eric H. (M)

Portugal
Lisbon—Pinheiro, Vitor P. (M)



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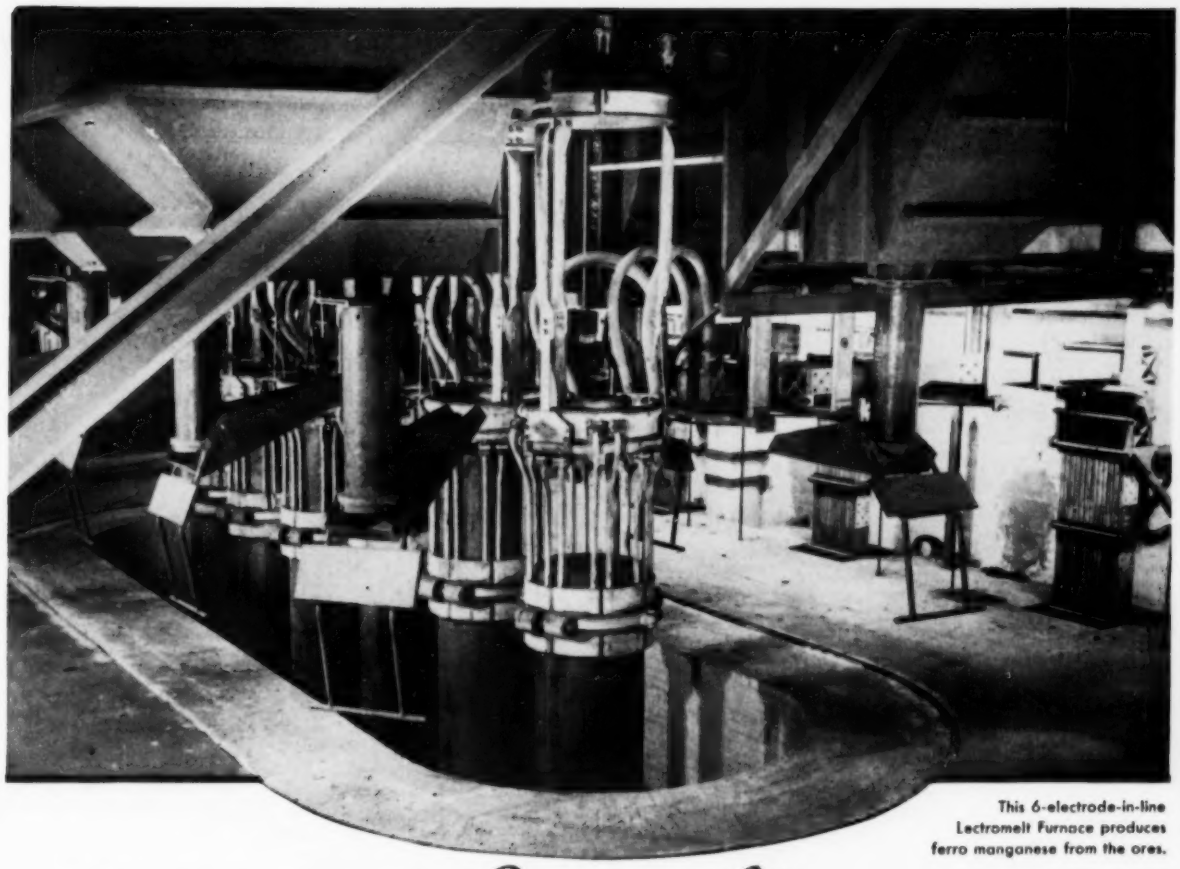

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Advantages of *Lectromelt** 6-electrode-in-line smelting furnaces...

Provide more uniform heat distribution and production. You can maintain almost any desired heat condition with minimum downtime.

You'll get maximum electrical efficiency . . . resulting in low power consumption per ton and high power factor.

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1. Electrodes equidistant from refractories at 14 places, instead of three places as in a circular furnace . . . avoid super-heated zones, make heat distribution uniform.

2. Three-phase power arrangement allows each pair of electrodes to operate at independent voltage settings, giving greater flexibility; permitting temperature increases, for example, of a viscous slag near the taphole before making a tap.

3. You can space electrodes for best operation by sliding electrode gear longitudinally . . . without shutting down furnace.

4. Furnace charge protects sidewalls, adds life to carbon or refractories.

5. Furnace is oblong; requires less space . . . it's mechanically easier to charge.

6. In-line electrodes permit simple monorail crane for adding sections easier in less time.

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*REG. T. M. U. S. PAT. OFF.

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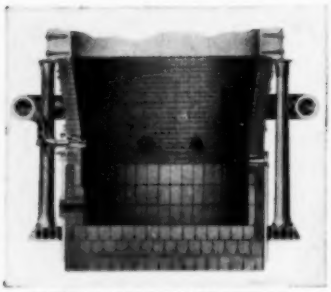
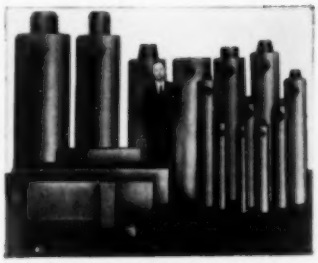
GRAPHITE SINTERING BOATS & TRAYS



CARBON BLAST FURNACE LININGS

GET MORE TONNAGE FOR LESS



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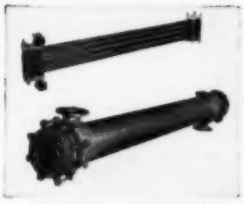

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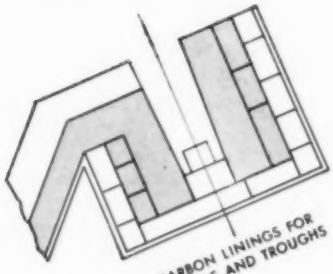

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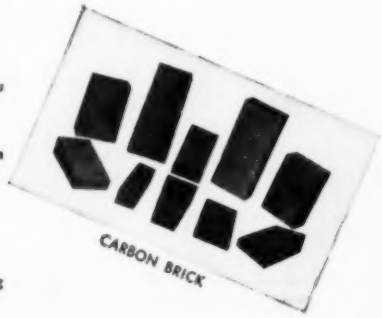

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